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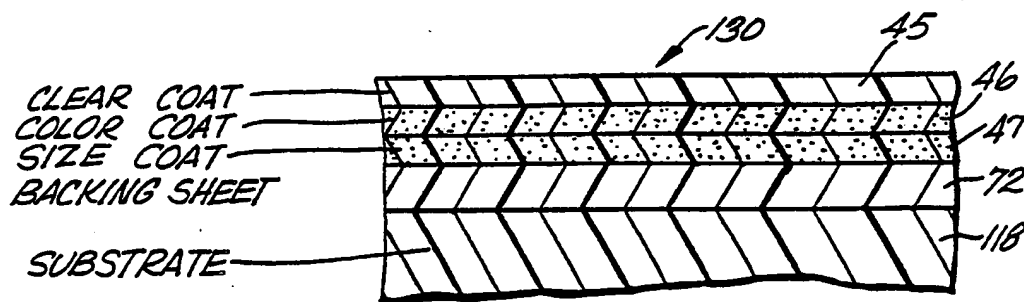
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁴ : B05D 1/00, 7/02, 5/06 B62D 29/04, B44C 3/04, 3/08 B44C 5/04		A1	(11) International Publication Number: WO 88/ 07416 (43) International Publication Date: 6 October 1988 (06.10.88)
(21) International Application Number: PCT/US88/00991 (22) International Filing Date: 25 March 1988 (25.03.88) (31) Priority Application Numbers: 031,984 162,917 (32) Priority Dates: 27 March 1987 (27.03.87) 2 March 1988 (02.03.88) (33) Priority Country: US (60) Parent Applications or Grants (63) Related by Continuation US 031,984 (CIP) Filed on 27 March 1987 (27.03.87) US 162,917 (CIP) Filed on 2 March 1988 (02.03.88) (71) Applicant (for all designated States except US): AVERY INTERNATIONAL CORPORATION [US/US]; P.O. Box 7090, Pasadena, CA 91109 (US). (72) Inventors; and (75) Inventors/Applicants (for US only) : SPAIN, Patrick, L. [US/US]; 5608 West 154th Ct., Lowell, IA 46356 (US). TRUOG, Keith, Lawson [US/US]; 1602 Sunnyslope Drive, Crown Point, IN 46307 (US).		(74) Agents: MAXWELL, Walter, G. et.al.; Christie, Parker and Hale, P.O. Box 7068, Pasadena, CA 91109-7068 (US). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), FR (European patent), GB (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), RO, SE (European patent), SU, US, US. Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	

(54) Title: DRY PAINT TRANSFER PROCESS AND PRODUCT



(57) Abstract

An automotive quality paint coat (44) is laminated to the exterior surface of a molded plastic car body member or panel (118). In one embodiment, the paint coat (44) includes an exterior clear coat (45) above a color coat (46). During processing, the clear coat (45) and color coat (46) are each coated on a temporary flexible casting sheet (42) and dried. A high gloss surface is transferred to the clear coat (45) from the casting sheet (42). The paint coat (44) is then transferred from the casting sheet (42) to a thin, semi-flexible thermoformable plastic backing sheet (72) by dry paint transfer-laminating techniques. The resulting laminate (70) is thermoformed into a complex three-dimensional shape of the car body member or panel. The preformed laminate (116) is then bonded to an underlying plastic substrate material, by injection-cladding techniques, for example, to form the finished article. The paint coat (44) has sufficient elongation to retain exterior automotive appearance and durability properties during thermoforming without deglossing. The backing sheet (72) absorbs defects in the substrate material so the paint coat retains its appearance and durability properties during the injection-cladding step. The finished article comprises a high gloss, defect-free paint coat on the exterior of a molded plastic car body member or panel. Solution-form polyvinylidene fluoride/acrylic paint systems have remarkably high combined gloss and distinctiveness-of-image levels, together with durability properties required for exterior automotive use.

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DRY PAINT TRANSFER PROCESS AND PRODUCTFIELD OF THE INVENTION

15 This invention relates generally to dry paint transfer techniques, and more particularly to the use of these techniques to produce exterior plastic car body members or panels with a paint coat applied in a separate production operation which can eliminate or greatly reduce the painting steps carried out in the manufacturing operations of a conventional automobile production plant.

20

BACKGROUND

25 Automotive design and manufacture present a unique set of problems in the selection of materials and processes used in the manufacture of automobile bodies. As a form of transportation, automobiles are unique because most buyers want a vehicle to have a certain individual styling. A recent trend in the automobile industry is toward production of distinctive vehicles

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1 styled to attract specific groups of consumers. This
change has required the car builder to shift production
from a few models manufactured in large volumes to a
larger number of more distinctive body styles. These
5 developments have demanded from the manufacturer both
styling flexibility and reasonable tooling costs for
each body style.

For many years, car body members and panels have
been made predominantly from sheet metal. However, car
10 builders now generally recognize that future use of
plastics for exterior car body members and panels,
rather than sheet metal, may provide a solution to
meeting the demand for more unique body styling and
reduced tooling costs. With the increasing concern for
15 weight-reduction, car builders have also turned their
attention to the use of plastics as an alternative to
heavier metal parts. For instance, certain exterior car
body parts of many automobiles now on the road are made
from lighter-weight plastic. These parts include
20 bumpers, rocker panels, fender extensions, window and
door moldings, and the like.

As reported in Plastics World, November, 1986, p.
30 et seq., a number of advanced corporate development
programs now in process are also seeking solutions to
25 the problem of commercially manufacturing from plastics
the larger exterior car body panels such as hoods,
roofs, deck lids, and in fact, the entire car body, if
possible. The concept of making a production car body
from a material other than sheet metal dates back to at
30 least as early as the mid-1950's, when the Chevrolet
Corvette was first manufactured with a fiberglass body.
Developments in plastic resin technology in recent years
have resulted in more sophisticated plastic materials of
higher impact strength than fiberglass. Polycarbonates
35 are an example. These developments in plastics

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1 technology have caused many plastics manufacturers, for
about the last decade or so, to seek solutions to the
problem of commercially producing the entire car body at
a reasonable cost from these later-developed high-
5 strength plastic materials. Recent development efforts
have also been directed toward producing plastic car
bodies from various alternative plastics molding
processes, including use of SMC (sheet molding
compounds) and RIM (reaction injection molding)
10 techniques.

Development of a production process for making
exterior car body members and panels from plastics
requires solutions to a number of technical problems.
These parts must be manufactured at reasonable costs for
15 tooling, assembly and materials. The end product also
must meet certain quality requirements. For instance,
the resulting car body panel must have structural
capabilities such as impact strength and resistance to
mechanical stress necessary to compete with sheet metal.
20 It must also have a paint coat with a defect-free and
durable exterior surface. An automotive quality paint
coat must meet certain specifications for a large number
of physical properties in order to be capable of use as
an exterior automotive paint coat. These properties
25 include gloss; distinctiveness-of-image; hardness;
abrasion resistance; weatherability such as UV
resistance; impact strength; thermal stability, namely,
resistance to extreme high and low temperatures;
gasoline and acid resistance; cleanability; adhesion to
30 the underlying car body panel; resistance to water and
humidity exposure; and hiding ability or opacity of the
paint coat.

In the past, a conventional production process for
applying an exterior paint coat to car bodies made of
35 sheet metal has involved transporting the preformed auto

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1 bodies to application lines in the plant where the car
bodies are dipped in paint, followed by transporting
them to a separate location for baking the paint coat
and waiting until the hardened paint coat dries
5 thoroughly. Most paint systems today are acrylic
enamels which are cross-linked into a hard, glossy,
durable paint coat during baking. Following painting,
the car bodies are transported back to the production
plant for further assembly operations. The painting of
10 plastic car body members has typically involved manually
spray painting the plastic parts in a separate painting
facility, followed by drying, and then transporting the
finished parts back to the assembly operation.
Conventional painting of sheet metal car bodies and
15 plastic parts is expensive and is a significant factory
problem with respect to environmental protection,
workers' safety, corrosion treatment, and waste
disposal. It is estimated that about one third of the
total capital investment in an automobile production
20 facility today is involved in painting car body members
and panels.

In recent years, metalized laminating techniques
have been used for forming a reflective, weather-
resistant metal surface on molded plastic automotive
25 trim parts. These techniques have not yielded plastic
trim parts with a paint-coated surface capable of
exterior automotive use. Such plastic trim parts have
experienced difficulties in maintaining reflectivity and
avoiding surface defects under mechanical impact and
30 environmental exposure.

New car body applications of molded plastic
materials can develop if the manufacturer can find a way
to commercially produce plastic car body panels with a
paint coat having the durability and appearance
35 properties necessary for exterior automotive use.

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1 Moreover, if in-mold painting or coating processes can
be developed as an alternative to conventional auto
painting, then auto assembly plants can be more compact,
and capital costs and environmental and safety problems
5 associated with conventional car painting at the factory
site can be avoided.

Many corporate product development efforts have
sought alternatives to conventional painting of molded
plastic exterior car body panels and parts, but without
10 any known success to date. A number of problems must be
overcome to develop an economical production-type paint
system and process for applying a paint coat capable of
exterior automotive use for molded plastic exterior car
body panels and parts so as to eliminate conventional
15 spray painting operations. For instance, use of the
cross-linked acrylic enamel paint systems which are
commonly baked on the sheet metal car bodies to produce
a tough, glossy finish cannot be used in painting
plastic car bodies because of temperature limitations.
20 One approach, which is the subject of this invention,
involves developing a paint-coated laminate which can be
used to replace the conventional painted finish on the
exterior of an automobile body. The laminate is made
from a paint coat applied to a casting sheet by paint
25 coating techniques. The dried paint coat is then
transferred from the casting sheet to a laminate panel
by dry paint transfer techniques. The coating operation
permits use of high temperature resistant paint systems
capable of producing a tough, glossy finish. The
30 laminate is later thermoformed into a complex three-
dimensional shape and then bonded or integrally molded
to an underlying plastic car body member or panel.
Injection-cladding techniques can be used to manufacture
a molded plastic part and simultaneously bond the
35 laminate to the exterior of the molded plastic part.

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1 A number of technical problems must be overcome in
order to use such a laminate in a thermoforming and
injection-cladding process, while maintaining a defect-
free painted surface with high gloss and durability
5 properties throughout the thermoforming and injection-
cladding steps. For instance, the laminate must be heat
and vacuum-formable into a complex three-dimensional
shape without cracking, deglossing, stress whitening or
creating other surface defects. A paint coat on such a
10 laminate can require a substantial amount of pigment in
order to provide the necessary color density or opacity
and distinctiveness-of-image. However, it has been
found that use of pigments in a paint coat can cause
deglossing of the surface when a paint-coated laminate
15 is thermoformed. Deglossing may even occur in a
nonpigmented clear coat during thermoforming.

In addition to surface gloss requirements, the
finished paint coat must be defect-free. Defects must
not be produced by the thermoforming step, and the
20 laminate also must be bonded or molded to the underlying
plastic substrate in a manner that hides any defects
that may be present in the substrate material.

Moreover, a finished paint coat may have a
reasonably high surface gloss, but still not have the
25 desired visual appearance known as distinctiveness-of-
image. This property relates to the mirror-like
character of the finish and is measured by the clarity
of an image reflected by the finished surface. It is
difficult, in a thermoforming operation, to produce an
30 exterior automotive paint coat with a high gloss level
and a high distinctiveness-of-image.

Durability properties are also critical in
producing a paint coat capable of exterior automotive
use. The paint coat must avoid exhibiting defects when
35 exposed to mechanical impact and avoid deterioration of

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1 the surface from exposure to chemicals and to the weather.

5 A paint system that produces the toughness or hardness necessary for exterior automotive use also must have the elongation properties and heat resistance necessary to allow thermoforming of the paint coat into complex three-dimensional shapes without cracking, deglossing, producing stress lines or other surface non-uniformities, or otherwise degrading the finish. Large
10 pigment levels also adversely affect the strength and alter elongation properties of the paint coat. In addition, reliable bonding of the paint coat to the laminate and bonding of the laminate to the underlying substrate material are essential.

15 Thus, the desired paint system should have a critical combination of many physical properties in order to produce a surface capable of exterior automotive use, while retaining desired surface characteristics after the laminating, thermoforming and
20 injection-cladding or molding steps have been carried out. However, some physical properties tend to be mutually incompatible in such a process. For instance, a paint system may have good qualities of durability such as hardness, toughness, weatherability and the
25 like; but the same paint system may not have sufficient elongation to be heat-formed into a complex shape without cracking or otherwise losing its durability properties. Other paint systems may degloss when heat-formed into a complex shape. Some paint systems have
30 sufficient elongation to permit thermoforming into the desired complex shape, but they are too soft and therefore lacking in the necessary hardness or durability properties.

35 In summary, there is a need for an economical production process for manufacturing highly contoured

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1 molded plastic exterior car body members or panels with
a laminated paint coat having both the durability and
the gloss and other appearance properties sufficient for
exterior automotive use. Laminating techniques for
5 applying a paint coat to such a molded plastic part can
provide a valuable alternative to conventional painting
of exterior car body members. Certain properties, such
as glass-smooth, defect-free surfaces and uniform paint
coats, are better produced by laminating techniques than
10 by conventional painting. Capital costs also can be
reduced and environmental problems can be alleviated.
Laminating techniques require, in addition, however, a
paint system and processing techniques capable of
producing and maintaining, throughout processing, the
15 durability and elongation properties, opacity, gloss and
distinctiveness-of-image levels, and defect-free surface
necessary for exterior automotive applications. The
present invention solves these problems.

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1 SUMMARY OF THE INVENTION

 Briefly, one embodiment of this invention provides a process for manufacturing a molded plastic article having a finished paint coat with surface properties meeting criteria for exterior automotive use. These include properties providing predetermined durability, gloss and other appearance characteristics in the finished paint coat. In this process, the paint coat is applied to a three-dimensionally shaped exterior surface of an intermediate laminate by a combination of paint coating, dry paint transfer-laminating, and thermoforming techniques. The thermoformed laminate then can be bonded to or molded to an underlying plastic substrate, for example, by injection-cladding techniques, with the paint coat maintaining properties sufficient for exterior automotive use throughout these processing steps. The invention is described herein in the context of a paint coat applied to the surface of a plastic car body member or panel, but the invention is also applicable to other articles of manufacture having a paint coat with properties similar to those required for exterior automotive use.

 Considering the application of the invention to a process for making a plastic exterior car body panel, a paint coat comprising a synthetic resinous material is coated in thin-film form onto a flexible, heat-resistant temporary casting sheet. The paint coat is dried on the sheet sufficiently to harden it and transfer a predetermined exterior surface gloss level from the casting sheet to the paint coat. The paint coat may comprise a clear coat and a separate pigmented color coat. The clear coat and color coat may be formed as separate thin-film coatings which are dried and then bonded to one another. The color coat, in combination with the clear coat, provides a composite paint coat

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1 having the durability, gloss and other appearance
properties necessary for exterior automotive use. The
paint coat is transferred to a semirigid, thermoformable
synthetic resinous backing sheet so that the paint coat
5 provides the exterior surface of the paint-coated
backing sheet. The laminate formed by the backing sheet
and the bonded paint coat is thereafter thermoformed to
produce a three-dimensionally shaped preformed laminate,
while still retaining durability, gloss and other
10 appearance properties necessary for exterior automotive
applications. The thermoforming step can produce
substantial elongation of the paint coat. The paint
coat is capable of elongating from about 50% to about
150%, or more, during thermoforming, without significant
15 loss of its exterior automotive durability, gloss and
other appearance properties. In a subsequent injection-
cladding step, for example, a synthetic resinous
substrate material is injection molded behind the
preformed paint-coated laminate to bond the laminate to
20 the substrate. This forms a molded plastic article with
a painted surface which retains the exterior automotive
surface characteristics. The substrate can be an
exterior body panel of a motor vehicle. The substrate
material normally may have a substandard surface finish,
25 but the backing sheet absorbs surface defects in the
substrate material during the injection-cladding step so
as to retain the minimum surface defect level and gloss
required of an exterior automotive paint coat.

In one embodiment, the paint coat comprises a
30 fluorinated polymer and acrylic resin-containing paint
system with thermoplastic properties. The relative
amounts of the fluorinated polymer and acrylic resin
components in the paint coat formulation provide a
sufficient level of resistance to deglossing and
35 sufficient elongation for the laminate to be

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1 thermoformed into complex three-dimensional shapes while
providing sufficient durability and appearance
properties for the finished product to be useful as an
exterior automotive body member or panel.

5 In one embodiment in which the paint coat comprises
an exterior clear coat and an underlying color coat
bonded to the clear coat, the clear coat can be formed
from a fluorinated polymer and acrylic resin-containing
10 coating. In this case, the clear coat can provide the
majority of the durability, gloss and other appearance
properties necessary for use as an exterior automotive
paint coat. The color coat also can comprise a thermo-
plastic fluorinated polymer and acrylic resin-containing
15 paint system. Other paint systems compatible with the
clear coat and the backing sheet also can be used.

In one form of the invention, the fluorinated
polymer component comprises polyvinylidene fluoride
(PVDF), and the acrylic resin component can be a
polymethyl methacrylate resin, a polyethyl methacrylate
20 resin, or mixtures thereof, including copolymers
thereof. One finished product having a surface capable
of exterior automotive use is made from a paint system
comprising from about 50% to about 70% PVDF and from
about 30% to about 50% acrylic resin, by weight of the
25 total PVDF and acrylic solids, exclusive of the pigment.

This invention also provides an exterior automotive
quality paint coat having unusually high gloss and
distinctiveness-of-image (DOI) along with other
durability properties sufficient for exterior automotive
30 use. This embodiment of the invention includes a
thermoformable laminate having a paint coat bonded to it
in which the paint coat, prior to casting on a casting
sheet, was prepared as a solution of vinylidene fluoride
in acrylic resin. The paint coat comprises at least a
35 clear coat of vinylidene fluoride and acrylic resin

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1 coated from solution, which produces thermoformed
laminates with high combined gloss and DOI levels. Good
combined gloss and DOI levels have been obtained
experimentally when the clear coat and pigmented base
5 coat both are prepared as a solution of vinylidene
fluoride in the acrylic resin. In one experimental test
of a finished car body panel, a 60° gloss level of
greater than about 75 gloss units and a DOI approaching
about 90 units were achieved.

10 Different forms of the invention are disclosed
herein. One embodiment comprises a thermoformable
laminate having a paint coat with properties capable of
use in forming an exterior automotive finish on a
plastic exterior car body panel. A further embodiment
15 of the invention provides a process for applying a paint
coat to an exterior body panel of a motor vehicle so
that the paint coat in its finished form has the dura-
bility, gloss and other appearance properties necessary
for exterior automotive use. Another embodiment of the
20 invention comprises a pressure-sensitive adhesive-backed
paint-coated laminate capable of use in automotive paint
coat repair.

Thus, the present invention provides a process and
articles of manufacture in which a laminated exterior
25 paint coat ultimately forms an exterior finish on a
highly contoured surface of a molded plastic article.
The paint coat has a sufficient combination of
elongation and resistance to deglossing to withstand
thermoforming without disrupting the high gloss surface
originally present, while retaining the durability and
30 appearance properties sufficient to be useful as an
exterior paint coat for a plastic car body panel.

These and other aspects of the invention will be
more fully understood by referring to the following
35 detailed description and the accompanying drawings.

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1 DRAWINGS

FIG. 1 is a semi-schematic perspective view illustrating an automobile which may have one or more of its exterior body members or panels made from a molded plastic substrate having a paint coat produced according to principles of this invention.

FIG. 2 is a front elevation view illustrating a rear window panel section of a motor vehicle in which an exterior paint coat is formed on the surface of the window panel according to principles of this invention.

FIG. 3 is a cross-section taken on line 3-3 of FIG. 2 for illustrating the complex three-dimensional shape of the paint coat transferred to the exterior surface of the window panel.

FIG. 4 is a schematic cross-sectional view illustrating one embodiment of a paint-coated carrier sheet used in the dry paint transfer-laminating steps of this invention. Film thicknesses are exaggerated in size and not to scale, for simplicity.

FIG. 5 is a schematic side elevation view illustrating a paint coating step of the process.

FIG. 6 is a schematic side elevation view illustrating a laminating step of the process.

FIG. 7 is a schematic cross-sectional view illustrating a dry composite paint coat transferred to a backing sheet during the laminating step. Film thicknesses are exaggerated in size and not to scale, for simplicity.

FIG. 8 is a schematic view illustrating a thermoforming step of the process in which a paint-coated laminate is heated prior to vacuum forming.

FIG. 9 is a schematic view illustrating another thermoforming step in the process.

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1 FIG. 10 is a schematic cross-sectional view illustrating a preliminary step in an injection-cladding step of the process.

5 FIG. 11 is a schematic cross-sectional view illustrating a substrate material injection-molded behind the thermoformed laminate in an injection mold.

10 FIG. 12 is schematic cross-sectional view illustrating the composite cross-sectional structure of the finished molded plastic article having exterior paint coat. Film thicknesses are exaggerated in size and not to scale, for simplicity.

15 FIG. 13 is a graph illustrating a general relationship between surface gloss and the relative amounts of polyvinylidene fluoride and acrylic resin contained in one embodiment of the paint coat.

20 FIG. 14 is a schematic cross-sectional view illustrating one embodiment of a laminate having a dry paint film and a pressure-sensitive adhesive backing for use in automotive paint coat repair, according to principles of this invention.

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1 DETAILED DESCRIPTION

 A paint coat with a surface capable of exterior automotive use is applied to a molded plastic article by a combination of paint coating, dry paint transfer-laminating, and thermoforming techniques for forming a paint-coated laminate which is then bonded to or molded to an underlying plastic substrate. The thermoformed laminate can be bonded to the substrate by injection-cladding techniques. The exterior automotive properties of durability, gloss and other appearance criteria are produced and maintained throughout the process.

 FIGS. 1 through 3 illustrate one embodiment of the dry paint transfer process and product in which an exterior automotive paint coat is transferred to an exterior body member or panel of an automobile 20. In the illustrated embodiment, the paint coat is transferred to the exterior surface of a rear window panel or molding 22 of the vehicle. The rear window molding can be injection-molded from a wood-filled synthetic resinous plastic substrate 24 which forms the structural portion of the panel. The paint coat 26 can be transferred to the exterior surface of the substrate by the paint coating, dry paint transfer-laminating, thermoforming and injection-cladding techniques described below. The paint coat 26 has properties useful in an exterior automotive paint coat, and these properties are also described in more detail below. Use of the process and article of this invention is described in the context of exterior car body members and panels, although other end uses of the process and article also are possible, without departing from the scope of the invention. For simplicity, exterior car body members or panels are referred to herein as car body panels.

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1 The plastic substrate material 24 can contain large
amounts of filler materials which can produce a normally
substandard surface on the substrate. In carrying out
the invention, the paint coat 26 is transferred to the
5 surface of the substrate so that any imperfections in
the underlying structural surface are absorbed by the
laminate, thus presenting a perfectly smooth,
unblemished paint coat having properties sufficient for
exterior automotive uses. The rear window molding
10 serves as an example of the type of highly contoured
exterior surface to which the paint coat can be
transferred. Referring to the rear window molding 22 in
FIGS. 2 and 3, the molding has a large oblong-shaped
window opening 28 with a wide border 30 having a highly
15 contoured exterior surface extending around the window
opening. The complexly shaped, multiple contour surface
includes a curved outer ridge 32 of tapered cross-
section extending around the periphery of the molding, a
longitudinally curved and narrow recessed region 34
20 extending inside the outer ridge, and a wide border
section 36 of raised elevation inside the recessed
region 34 extending around the entire periphery of the
window opening. The wide border region 36 is at the
same elevation as the surface of a wide end member 38 at
25 one of the window opening. An inside edge 40 of the
wide border section 36 has a tapered cross-sectional
thickness and extends around the inside of the window
opening. As represented in FIGS. 2 and 3, the exterior
automotive paint coat 26 is adhered to the complexly
30 shaped exterior surface of the rear window molding, but
the paint coat also can provide a durable, high gloss
exterior surface useful on other car body panels of
various irregularly shaped three-dimensional surface
configurations, as well as other articles of
35 manufacture.

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1 Paint Coat

 The process first includes the step of coating a paint coat, or a portion of a paint coat, onto one or more temporary carrier sheets. FIG. 4 illustrates one
5 embodiment of a paint-coated carrier 41 which includes, in combination, a flexible, foldable, heat-resistant, self-supporting carrier sheet 42, also referred to in the art as a casting film; and a transferable, adherent, flexible paint coat 44 coated onto one surface of the
10 carrier. The paint coat 44 is a non-self-supporting, flexible synthetic resinous dry film-form coating. The paint coat 44 can comprise a combination exterior clear coat and a color coat, or a combination exterior clear coat and a tint coat; or the paint coat may comprise a
15 single dry film-form coating of a pigmented synthetic resinous material having the exterior automotive properties described below. In a presently preferred form, the paint coat 44 includes a clear coat 45 coated over the carrier and dried, and a color coat 46 on the
20 dried clear coat. The color coat can be coated onto the dried clear coat. Alternatively, the clear coat and the color coat can be separately coated onto corresponding carrier sheets and dried on their respective carriers. The color coat then can be later bonded to the clear
25 coat. The combination clear coat and color coat are referred to herein as the paint coat 44, or a composite paint coat, for simplicity.

 The paint-coated carrier also optionally can include a size coat 47 coated on the dried color coat.
30 The size coat provides adhesion to a backing sheet in a subsequent laminating step. In one embodiment, described below, a thermoplastic polyolefin backing sheet is used, and a thermoplastic chlorinated polyolefin size coat provides superior adhesion between
35 the paint coat and the backing sheet.

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1 The carrier sheet 42 is preferably a polyester
casting film having a high gloss surface 48. The
carrier can be a polyester film such as Mylar (a
5 trademark of DuPont), American Hoechst 3000 polyester
film, or the like. The preferred film thickness of the
carrier sheet is about two mils. Polyester films are
preferred because the high gloss surface 48 is capable
of transferring a high gloss level to a surface 49 of
10 the clear coat 45 in contact with the carrier, where the
transferred gloss level is sufficient for exterior
automotive use. Alternatively, the coatings can be cast
on a polished metal belt. If the color coat is cast on
a separate carrier sheet, the surface gloss imparted to
15 the color coat from the carrier is not critical. The
polyester carrier film has a sufficiently high heat
resistance to resist axial elongation under the
temperatures applied during subsequent paint coat drying
and laminating steps. The clear coat may be applied to
20 the polyester carrier film without a release coat on the
high gloss surface 48 of the carrier. This can avoid a
separate coating, which might detrimentally affect
transfer of the high gloss surface from the carrier to
the surface 49 of the clear coat. The formulation of
25 the clear coat is such that the clear coat can be easily
transferred from the carrier sheet and can replicate the
high gloss surface of the carrier after the clear coat
dries and after subsequent dry paint transfer-laminating
steps in which the paint coat is transferred from the
carrier to a laminate described below.

30 As an optional step; a thin film of wax (not shown)
can be coated onto the carrier sheet and dried, followed
by coating the clear coat 45 over the thin film of wax.
The wax is coated in a film thickness (less than 0.01
mil and preferably 0.001 mil) that avoids any adverse

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1 effect on the clear coat replicating the surface gloss
of the carrier.

5 The clear coat 45 is a transparent or substantially
transparent thermoplastic synthetic resinous coating
composition coated in thin-film form onto the surface of
the carrier sheet in a liquid state. Heat is later
applied to the clear coat to dry it, without cross-
linking the resin, while the clear coat is on the
carrier. The preferred dry film thickness of the clear
10 coat is about 0.5 to about 1.5 mils. Preferably, the
clear coat is coated onto the carrier sheet by a reverse
roll coating process illustrated in FIG. 5, although the
clear coat can be applied by gravure printing, or other
conventional coating techniques. Referring to the
15 reverse roller coating process of FIG. 5, the clear
coat lacquer 46 is contained in a coating pan 50 having
a lacquer inlet 52 in the main portion of the pan and a
lacquer drain 54 on an opposite side of a weir 56. An
applicator roll 58 rotates to pick up the lacquer from
20 the pan and coat it onto a previously uncoated polyester
film 42 which passes over a guide roll 60 and then
passes between the applicator roll and a rubber backup
roll 62. A metering roll 64 adjacent the applicator
roll rotates in the same direction as the applicator
25 roll. A doctor blade 66 wipes the surface of the
metering roll to properly control the thickness of the
coating on the applicator roll. The adjustable gap
between the metering roll and the applicator roll
controls the thickness of the coating on the surface of
30 the applicator roll. The coating picked up by the
applicator roll is then coated onto the polyester film
42 as the film passes into contact with the reverse-
rotating applicator roll. The applied coating on the
film is shown at 68. The coated film then passes to a
35 drying oven.

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1 The clear coat is dried at oven temperatures in the
range from about 250°F to about 400°F. Preferably, the
clear coat is dried in multiple zones spaced apart along
the long axis of the paint-coated carrier, in line with
5 the reverse roll coater. A preferred drying technique
involves use of three heating zones, with a
progressively higher temperature applied in each
successive zone. The solvent gases contained in the
clear coat are essentially all driven off in the multi-
10 stage drying process. The same multi-stage drying
process is used for drying the color coat 46 and the
size coat 47. The polyester carrier is resistant to
heat at temperatures greater than about 450°F, so the
carrier does not deform during the drying step. The
15 polyester carrier film thickness of about two mils
assists the film in resisting elongation during the
drying steps. This ensures a high gloss level being
replicated by the surface 49 of the dried clear coat
from the high gloss surface 48 of the carrier. This
20 also makes it possible to use high temperature-
resistant, high gloss paint systems which cannot be
applied to and dried on plastic substrates directly
because of temperature limitations of the plastic
materials.

25 The clear coat formulation produces a dry film-form
exterior film which, in combination with the underlying
color coat, produces a composite paint coat having
properties useful as an exterior automotive paint coat.
Such a paint coat is principally characterized by a
30 combination of exterior automotive durability properties
and gloss and other appearance properties of the
finished paint coat. The specifications for a paint
coat for exterior automotive use, as defined herein,
include the mechanical properties of hardness; abrasion
35 resistance; thermal stability, including heat

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1 resistance; resistance to gasoline and acids;
cleanability; adhesion; certain weatherability
properties such as UV resistance and resistance to water
and humidity exposure; and impact strength. For
5 simplicity, these properties are referred to
collectively herein as "durability properties".

Weatherability, which is measured, in part, by UV
resistance properties, is a durability property commonly
used in the art to define standards for an exterior
10 automotive paint coat. To measure UV resistance can
require long-term exposure testing of the paint coat,
for a period of two years in one test method. Certain
long-term UV tests of the paint coat of this invention
have not been completed to date, but other short-term
15 accelerated UV resistance and weatherability tests of
the paint coat have been completed and are described
below.

In addition to durability properties, the
specifications for an exterior automotive quality paint
20 coat also include tests to measure the visual appearance
qualities of the finished surface. These criteria
include gloss, distinctiveness-of-image (DOI), dry film
thickness and hiding ability or opacity of the paint
coat. These properties are referred to collectively
25 herein as "gloss and other appearance properties".

Thus, a paint coat can have a combination of pre-
determined physical properties that collectively define
whether the paint coat is capable of use as an exterior
automotive paint finish. Generally, the paint coat of
30 this invention, in dry film-form, provides a combination
of the above-described durability and appearance prop-
erties, including gloss, which enables the paint coat to
function as an exterior automotive paint coat.

The criteria used to define whether a paint coat is
35 sufficient for exterior automotive use are not uniform

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1 throughout the automobile industry. Certain standards
can vary from one auto manufacturer to the next, and
from one car model to the next for a given auto manufac-
turer. Most criteria used to define an exterior
5 automotive quality surface for the process of this
invention have been adopted from specifications and test
methods used in certain General Motors Fiero and Pontiac
Grand AM test programs. These criteria are disclosed
herein as an example of techniques that can be used to
10 measure whether a paint coat has sufficient properties
for exterior automotive use, although other combinations
of test criteria and test methods can also be used for
this purpose. The specifications and test methods for
measuring the properties of the exterior automotive
15 paint coat of this invention are described in detail
below.

In addition to the properties of durability and
appearance, the clear coat formulation also imparts to
the composite paint coat sufficient elongation at
20 thermoforming temperatures to enable the paint coat to
be thermoformed into complex three-dimensional shapes
without deglossing of the clear coat and without
reducing any durability property below that required for
an exterior automotive surface. In one embodiment, the
25 paint coat is thermoformed at temperatures from about
280°F to about 450°F. A laminate having the clear coat
as its exterior surface is capable of being thermoformed
at these temperatures while maintaining the durability
and appearance properties of the composite paint coat.
30 Elongation of the paint coat can be substantial when
forming the complex three-dimensional shapes of the
finished article. Elongation of the clear coat (and the
composite paint coat) can be greater than about 50%, and
often greater than 100%, to form a highly contoured
35 finished article. Plastic car body members and panels

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1 often require such deep draw forming. The clear coat
also is capable of maintaining the durability and
appearance properties of the paint coat during a
subsequent injection molding step.

5 The clear coat is formulated from a transparent
thermoplastic (non-cross-linked) synthetic resinous
coating composition. The thermoplastic properties allow
the clear coat, in dry film-form, to soften and deform
and be vacuum-formable at thermoforming temperatures,
10 while still retaining exterior automotive durability
properties, gloss and other appearance properties after
the heated and three-dimensionally shaped film-form
coating returns to its stable or hardened condition. In
dry film-form, the clear coat has an extensibility in
15 the range from about 40% to about 150% or more, at a
film thickness from about 0.5 to about 1.5 mils, and at
thermoforming temperatures from about 280°F to about
450°F.

In one embodiment, the clear coat comprises a blend
20 of a thermoplastic fluorinated polymer and an acrylic
resin. The clear coat preferably contains the fluori-
nated polymer and acrylic resin as its principal
components. The fluorinated polymer component is
preferably a thermoplastic fluorocarbon such as
25 polyvinylidene fluoride (PVDF). The fluorinated polymer
also can include copolymers and terpolymers of
vinylidene fluoride. One thermoplastic fluorocarbon
useful in the clear coat is the polyvinylidene fluoride
known as Kynar, a trademark of Pennwalt Corp. This
30 polymer is a high molecular weight (400,000) polymer
which provides a useful blend of durability and chemical
resistance properties. Generally, a high molecular
weight PVDF resin, with a weight average molecular
weight of about 200,000 to about 600,000 is used.

35

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1 The acrylic resin component of the clear coat can
be a polymethyl methacrylate, or a polyethyl
methacrylate resin, or mixtures thereof, including
methacrylate copolymer resins, and minor amounts of
5 other comonomers. The clear coat also can include minor
amounts of block copolymers and/or compatibilizers to
stabilize the blended PVDF and acrylic resin system and
provide compatibility between films.

10 In one embodiment, a principal component of the
acrylic resin contained in the clear coat is a medium
molecular weight polymethyl methacrylate resin such as
Elvacite 2010, a trademark of DuPont. (In all further
references to Elvacite resins herein, it should be noted
15 that Elvacite is a trademark of DuPont for a group of
its acrylic resins.) In another embodiment, a principal
component of the acrylic resin for the clear coat can be
a high molecular weight polyethyl methacrylate resin
such as Elvacite 2042. The acrylic component of the
clear coat also can comprise a mixture of Elvacite 2010
20 and a medium-to-high molecular weight polymethyl meth-
acrylate resin such as Elvacite 2021. In a further
embodiment, the acrylic resin component can comprise
Elvacite 2042 and a low molecular weight polyethyl
methacrylate resin such as Elvacite 2043. Other similar
25 combinations of acrylic resins, their homopolymers and
copolymers, may be used as a component of the clear
coat. Generally, the acrylic resin component has a
relatively high weight average molecular weight of about
50,000 to about 400,000.

30 The PVDF and acrylic-based clear coat formulation
can be prepared as a solution of PVDF in the acrylic
resin and solvent. Experimental tests of finished car
body panels, in which the paint coat has been prepared
from a solution of PVDF in acrylic resin, have
35 demonstrated high levels of gloss and distinctiveness-

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1 of-image. The experimental text results are described
in Example 11 below.

5 The PVDF and acrylic-based clear coat formulation
also can be prepared as a dispersion of the PVDF in a
solution of the acrylic resin. In one embodiment, the
clear coat formulation can be prepared by mixing the
acrylic resin with a suitable organic solvent and
applying heat to dissolve the resin. The mixture is
then allowed to cool sufficiently before adding the PVDF
10 component so that the PVDF will not dissolve, but will
be maintained as a dispersion in the acrylic-solvent
based mixture. By maintaining the PVDF component as a
dispersion in the clear coat, solvent evaporation during
drying of the clear coat can be improved.

15 A preferred composition of the dried clear coat
comprises from about 50% to about 70% PVDF, and from
about 30% to about 50% acrylic resin, by weight. In
some instances the maximum content of the PVDF component
is about 65%, with the balance essentially comprising
20 the acrylic resin. These solids ranges are based on the
relative proportions of the PVDF and acrylic components
only in the clear coat formulation. Other minor amounts
of solids, such as UV stabilizers, block copolymers and
compatibilizers also may be contained in the clear coat
25 formulation.

In one embodiment, a successful experimental car
body panel having exterior automotive surface properties
was produced from a paint system in which the dried
clear coat consisted essentially of about 50% PVDF and
30 about 50% polymethyl methacrylate resin, by weight.
This clear coat provided high gloss (after
thermoforming) and good exterior automotive properties
of appearance and durability. In another successful
experimental car body panel having good exterior
35 automotive appearance and durability properties,

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1 including gloss, the dried clear coat consisted essentially of about 65% PVDF and about 35% polyethyl methacrylate resin, by weight.

5 The acrylic resin component of the clear coat is desirable because of its compatibility with the PVDF in dry film form. The acrylic component is added to the PVDF in an amount that prevents deglossing of the finished clear coat during thermoforming. The acrylic resin is also added in an amount that yields a
10 transparent clear coat in dry film form. Generally speaking, transparency and distinctiveness-of-image of the composite paint coat increase in proportion to the amount of acrylic resin added to the PVDF-acrylic system. It has been determined that a pure PVDF clear
15 coat has reasonably good properties of durability and elongation, but such a 100% PVDF coating is not normally transparent and it deglosses excessively when heated to normal thermoforming temperatures. When sufficient acrylic resin is added to the PVDF component, the
20 resulting clear coat becomes reasonably transparent and can resist deglossing at thermoforming temperatures. Increased transparency of the clear coat improves the gloss level of the finished clear coat. The acrylic resin is also combined with the PVDF in an amount that
25 maintains sufficient elongation to allow the clear coat (and the color coat to which it is bonded) to be thermoformed (as part of the laminate described below) into complex three-dimensional shapes, while retaining the exterior automotive durability properties and appearance
30 properties, including gloss, of the finished paint coat. It has been determined that a dry film-form PVDF-acrylic-based clear coat containing more than about 35% acrylic resin and less than about 65% to 70% PVDF, by weight of the total PVDF and acrylic solids, avoids
35

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1 deglossing during thermoforming while achieving
sufficient elongation.

It is believed that deglossing of a PVDF and
acrylic resin-based clear coat, in some instances, can
5 be caused by crystallization of the clear coat as it
cools down after thermoforming. Greater crystallization
of the PVDF-acrylic-based clear coat also is believed to
be caused, at least in part, by proportionately higher
thermoforming temperatures. Addition of the acrylic
10 resin to the PVDF in the clear coat formulation may
prevent crystallization of the PVDF in cool-down from
thermoforming at normal thermoforming temperatures. Use
of polymethyl methacrylate as the predominant component
of the clear coat acrylic resin may be desirable because
15 it produces a higher gloss level than polyethyl
methacrylate. It is believed that the higher gloss
results from a slower rate of crystallization of the
polymethyl methacrylate during cooling. It is also
believed that deglossing, in certain instances, may be
20 caused by microcracking of the clear coat surface during
thermoforming. Use of a certain amount of softer
acrylic resin than polymethyl methacrylate, such as
polyethyl methacrylate, may in some instances produce a
high gloss surface of the clear coat after
25 thermoforming, particularly in combination with lower
thermoforming temperatures.

To the extent that deglossing of the clear coat may
be caused by non-uniform coalescence of the PVDF
component in the resin system, it is believed that this
30 problem can be overcome by a more uniformly blended
dispersion of the PVDF in the acrylic resin or use of a
solution-based system.

The PVDF component of the clear coat is desirable
because of the exterior automotive durability properties
35 and the elongation properties it provides in the

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1 resulting clear coat, particularly in combination with
the acrylic resin component. The PVDF component also
provides good weatherability properties in the finished
paint coat. It has been determined that a pure
5 thermoplastic acrylic resin clear coat can provide good
hardness or toughness characteristics, but it lacks
weatherability. A pure acrylic resin clear coat also
creates difficulties in separating from the injection
10 mold after the injection-cladding step. A cross-linked
thermoset acrylic resin commonly used as an exterior
auto paint is not useful in the process of this
invention. When thermoformed, it shatters or cracks
when a vacuum is drawn on the laminate to which it is
coated. A dry film-form PVDF and acrylic resin-
15 containing clear coat having from about 30% to about 50%
acrylic resin (by weight of the total PVDF-acrylic-based
solids) has sufficient elongation to allow proper
thermoforming and injection-cladding, while maintaining
the exterior automotive durability, gloss and other
20 appearance properties of the finished composite paint
coat.

The color coat 46 is bonded to the clear coat after
the clear coat has been dried on the carrier sheet. The
color coat can be coated onto the dried clear coat, or
25 the color coat can be coated onto a separate polyester
casting film, dried, and later transferred from the
casting film to the clear coat. In either case, the
color coat is preferably applied to the casting film by
reverse roller coating techniques similar to those
30 illustrated in FIG. 5. A preferred dry film thickness
of the color coat is in the range of about 0.5 to about
1.5 mils. The color coat comprises a thermoplastic
synthetic resinous coating composition containing a
sufficient amount of pigment to provide the appearance
35 necessary for exterior automotive use in the finished

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1 article. More specifically, the color coat contains a
sufficient amount of pigment so that the composite paint
coat maintains sufficient opacity and distinctiveness-
of-image and avoids stress whitening throughout the
5 thermoforming step so to function as an exterior
automotive paint coat. The resinous material contained
in the color coat functions in combination with the
clear coat to produce the required exterior automotive
surface for the finished paint coat. That is, although
10 the clear coat provides the exterior surface portion of
the finished paint coat, the exterior automotive
properties of the finished surface are not controlled
solely by the clear coat formulation. The underlying
color coat can affect durability properties of the
15 finished paint coat, for example. Abrasion resistance
is an example of a mechanical property enhanced by a
tougher color coat in combination with the exterior
clear coat. Weatherability of the finished paint coat
also is influenced by the color coat formulation as well
20 as the clear coat. The color coat also comprises a
resinous material which is capable of sufficient
elongation at thermoforming temperatures so as to not
disrupt the exterior automotive properties of the
finished paint coat.

25 The color coat is preferably dried by passing it
through the same multiple heating zones used in drying
the clear coat. Drying temperatures in each of the
zones are progressively increased and can be at about
the same temperatures as those used for drying the clear
coat. Preferably, similar resinous components with
30 mutually compatible solvents are used in the clear coat
and color coat so that adhesion between the clear coat
and color coat is produced without requiring additional
stabilizers or additives. The color coat composition is
35 preferably a synthetic resinous coating composition

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1 having thermoplastic properties similar to the clear
coat. Although the color coat alone does not
necessarily require all of the exterior automotive
properties of durability and appearance, in order to
5 produce a useful composite paint coat, a color coat
composition (exclusive of the pigment contained in the
coating) having most of the desirable exterior
automotive durability properties is preferred. In one
embodiment, the color coat comprises a blended thermo-
10 plastic fluorinated polymer and acrylic resin-containing
paint system. This paint system can be similar to the
PVDF and acrylic-based coating used in the clear coat.
The fluorinated polymer component also can include
copolymers and terpolymers of vinylidene fluoride. The
15 color coat formulation can be prepared by mixing the
acrylic component with suitable organic solvents and
applying heat to allow the acrylic resin to dissolve.
In a preferred embodiment the PVDF component is
dissolved in the acrylic resin solution, although the
20 PVDF can be maintained as a dispersion in the acrylic-
based system. The pigment is then added to the PVDF-
acrylic composition. Preferably, the composition of the
dried color coat (the PVDF and acrylic-based solids,
exclusive the pigment) comprises from about 50% to about
25 70% PVDF and from about 30% to about 50% acrylic resin,
by weight of the total PVDF and acrylic solids. In a
preferred dispersion formulation, the dried color coat
comprises about 65% PVDF and about 35% acrylic resin, by
weight. The preferred acrylic component for the color
30 coat is a polyethyl methacrylate resin such as Elvacite
2042 or Elvacite 2043, or mixtures thereof. The
relatively higher amount of PVDF in the color coat
produces a softer film and therefore enhances elongation
properties.

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1 The color coat may contain a substantial pigment
level in order to provide sufficient opacity to maintain
desirable coloration in the finished article. In a
highly contoured three-dimensionally shaped article, a
5 large amount of pigment may be necessary for hiding,
following subsequent thermoforming steps. For most
colors, a pigment level from about 3% to about 30%, by
weight of the solids contained in the coating, also
referred to as the pigment-to-binder ratio, produces the
10 desired opacity in the finished paint coat. The amount
of pigment used varies depending upon the color. For a
red color coat used in an experimental car body panel,
for example, a pigment level of about 23%, by weight of
the total solids, was used. For a black color coat
15 using carbon black pigment in an experimental car body
panel, about 3% to 5% pigment was used.

 The pigment contained in the color coat can affect
exterior automotive properties. For instance, if the
color coat is applied to a laminate as a single paint
20 coat, or is applied to the laminate as an exterior paint
coat, the pigment contained in the coating can cause the
color coat to degloss during thermoforming of the
laminate. (Under these circumstances, the same coating
applied as a clear coat may not degloss during the same
25 thermoforming step.) It has been discovered that a
finished paint coat with a high gloss level can be
produced with a non-deglossing exterior clear coat
applied over a color coat which otherwise deglosses by
itself during thermoforming. Stated another way, a
30 color coat which normally deglosses as an exterior coat
may be used as an underlying color coat for an exterior
clear coat, if the clear coat can, following
thermoforming, produce the gloss necessary for exterior
automotive use.

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1 As to the deglossing phenomenon, it has been
discovered that an otherwise high gloss exterior surface
of a color coat, applied to a laminate in a flat
(planar) coating of uniform thickness usually deglosses
5 when the laminate is thermoformed into a complex three-
dimensional shape. It is believed that such deglossing
is caused by the particles added to the coating as
pigment penetrating the exterior surface of the coating
during the softening and elongation that occur during
10 thermoforming. It has also been discovered that such
deglossing can be overcome by coating (or laminating)
the exterior clear coat over the color coat at
sufficient film thickness that the clear coat can act as
a barrier to prevent the color coat pigment particles
15 from migrating from the color coat through the clear
coat and penetrating the surface of the clear coat
during the thermoforming step.

The high pigment level in the color coat also can
affect mechanical properties of the coating, such as
20 durability and elongation. Generally, the high level of
pigment contained in the color coat reduces elongation
of the coating. The pigment also can reduce the
strength or hardness of the coating. A color coat which
may, by itself, not have all of the durability
25 properties of an exterior automotive paint coat, can
still be useful in the finished article. However,
elongation properties are critical because the color
coat should not inhibit elongation of the clear coat
during thermoforming. If the amount of PVDF component
30 in the color coat is at least about the same or greater
than the amount of the acrylic component in the color
coat, elongation properties of the color coat are
enhanced. In addition, the acrylic component of the
color coat formulation can be a high molecular weight,
35 high-strength resin to add back to the color coat the

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1 hardness or strength characteristics lost by the
addition of the pigment to the color coat. The greater
amount of PVDF in the color coat also can improve
weatherability of the finished paint coat.

5 Thus, the desired color coat formulation provides
the appearance and durability properties which, in
combination with the clear coat, produce a composite
paint coat having the properties suitable for exterior
automotive use. The color coat also retains sufficient
10 elongation to be thermoformed in combination with the
clear coat so that the durability and appearance
properties, including gloss, of the finished paint coat
are not degraded during thermoforming. In one
embodiment, an experimental car body panel was made from
15 a color coat having PVDF in the range of about 50% to
about 70%, and a high molecular weight polyethyl meth-
acrylate resin in the range of about 30% to about 50%,
by weight of the total (non-pigment) solids. This com-
bination produced durability and appearance properties,
20 including gloss, in the finished paint coat sufficient
for exterior automotive use.

As an alternative to the PVDF and acrylic resin
combination, the color coat also can contain other
formulations. It is believed that a flexible pure
25 acrylic resin with the required elongation properties,
or certain softer acrylic copolymers or acrylic
dispersion lacquers having sufficient elongation and
durability properties (especially weatherability) also
can be useful as a color coat formulation. It is also
30 believed that certain urethanes and vinyl compositions
such as polyvinyl chloride can provide binders for
acceptable color coats. Use of a separate color coat
not containing a fluorinated polymer such as PVDF can
reduce the cost of the finished paint coat.

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1 Although the paint coat has been described in
relation to a clear coat and a separate color coat, the
paint coat of this invention also may be produced as a
single pigmented thermoplastic synthetic resinous
5 coating, with the pigment highly dispersed in the
coating so that deglossing upon thermoforming is
resisted. Alternatively, a clear coat having the
required durability and appearance properties may be
used in combination with an underlying coating or other
10 substrate material which provides the coloration and
other properties necessary for the combination to
produce a finished paint coat suitable for exterior
automotive use.

15 The size coat 47 is next coated onto the dried
color coat, either when the color coat is coated on the
clear coat, or when the color coat only is coated on a
separate casting sheet. The size coat bonds the paint
coat to the backing sheet used in the laminating step
described below. The size coat comprises any synthetic
20 resinous material which is heat-activated from the
subsequent laminating step to bond the paint coat to the
backing sheet. The preferred dry film thickness of the
size coat is from about 0.1 to about 1.0 mil. The size
coat is preferably applied as a thermoplastic and dried
25 in the same multi-stage drying step used in drying the
clear coat and the color coat. The size coat is dried
at a temperature which evaporates the solvent without
cross-linking the resin. The size coat composition can
vary depending upon the composition of the color coat
30 and the backing sheet to which the paint coat is bonded.
For a PVDF-acrylic-based paint coat, an acrylic resin-
based size coat is preferred for suitable bonding of the
paint coat to the backing sheet. In one embodiment, in
which the paint coat is adhered to a backing sheet made
35 of acrylonitrile-butadiene-styrene (ABS), the size coat

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1 comprises a polymethyl methacrylate resin such as
Acryloid A-101 (a trademark of Rohm and Haas Co.)
dissolved in a suitable solvent. In another embodiment
in which the backing sheet is a thermoplastic
5 polyolefin, the size coat preferably comprises a
chlorinated polyolefin.

Transfer to Thermoformable Backing Sheet

10 The paint-coated carrier illustrated in FIG. 4 is
next laminated to a thermoformable backing sheet by dry
paint transfer-laminating techniques. The laminating
step is illustrated in FIG. 6. FIG. 7 schematically
illustrates a thermoformable laminate 70 formed after
the dry paint transfer-laminating step. The laminate 70
15 includes the composite paint layer 44 (clear coat and
color coat) adhered to a backing sheet 72 by the size
coat 47. The backing sheet is preferably a semirigid,
self-supporting, thin, flat sheet of a synthetic
resinous material. The backing sheet is made from a
20 material which is compatible with an injection-molded
plastic material later used to form the structural
substrate base of the finished article. Preferably, the
backing sheet is made from the same or substantially the
same polymeric material as the substrate base of the
25 finished article. The backing sheet also is made from a
material having a thickness capable of thermoforming
into a complex three-dimensional shape, along with the
adhered composite paint coat, without disrupting the
exterior automotive properties of the paint coat. The
30 material from which the substrate is molded can contain
a substantial amount of filler and therefore can produce
an imperfect surface on an article molded from the sub-
strate material. The laminate 70 is adhered to the
otherwise imperfect surface of the molded substrate to
35 improve the surface characteristics of the substrate

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1 panel and produce an outstandingly smooth controlled
exterior automotive finish. The multi-layered article
in its finished form comprises a high performance
essentially defect-free, three-dimensionally shaped
5 paint coat with exterior automotive properties in
combination with the backing sheet 72, which provides a
buffer layer between the substandard surface of the
substrate and the finished paint coat. The backing
sheet material minimizes the surface imperfections
10 transmitted to the paint coat. The preferred material
from which the backing sheet is made is ABS. A
preferred ABS material is Borg Warner's Cycolac L.S.
Thermoplastic polyolefins (TPO's) including
polypropylenes and polyethylenes also may be used, as
15 well as polyesters or an amorphous nylon, such as Bexloy
C-712, a trademark of DuPont. Use of TPO backing sheets
and substrates in a composite structure is described in
greater detail below. The thickness of the backing
sheet can vary, but generally it is necessary for the
20 backing sheet to have a sufficient thickness to isolate
or absorb imperfections in the surface of the underlying
substrate while presenting a perfectly smooth upper
surface of the paint coat. The backing sheet is also
not so thick that it would otherwise disrupt the
25 elongation characteristics of the laminate during the
subsequent thermoforming step. A desirable range of
thickness of the backing sheet is believed to be from
about 10 to 30-40 mils, with 20 mils being a preferred
thickness for an ABS sheet, for example.

30 The laminating step is best understood by referring
to the schematic view of FIG. 6, in which the paint-
coated carrier 41 is shown stored on a top unwind roll
74 and a flexible 20 mil thick ABS backing sheet 72 is
stored on a bottom unwind roll 76. The paint-coated
35 carrier, in one embodiment, comprises the clear coat and

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1 color coat on a single flexible casting sheet. The
paint-coated casting sheet 41 is passed around a drum
77, and the backing sheet 72 passes around a drum 78.
The carrier and backing sheet then pass between a heated
5 laminating drum 79 and a rubber backup roll 80. The
laminating drum 79 is preferably made of steel and is
preferably operated at a temperature of about 400° to
425°F. It is pressed into contact with the overlapping
10 sheets to heat them to a temperature sufficient to
activate the adhesive in the size coat and press the two
sheets into contact with each other to bond the paint
coat to the backing sheet. The rubber backup roll 80 is
pressed into contact with the laminating roll,
15 preferably at a pressure of about 300 pounds per lineal
inch. The slow speed at which the sheets travel during
laminating ensures that the resulting laminate 70 is
heated to a temperature approaching the temperature of
the laminating drum. This softens the backing sheet
20 material somewhat as well as activating the heat-
activated size coat to ensure a complete bond between
the paint coat and the backing sheet. The polyester
carrier sheet of the paint-coated carrier has a heat-
resistance well above laminating temperatures so the
25 carrier sheet resists elongation during the laminating
step. Following the bonding step, the flexible paint-
coated laminate 70 is then passed around one or more
chill rollers 82 for cooling the laminate to room
temperature. The laminate 70 then passes onto a
30 laminate rewind drum 84. The carrier sheet is stripped
away from the laminate prior to the subsequent
thermoforming step. This leaves a smooth, defect-free
high gloss exterior surface on the clear coat which
replicates the high gloss surface present on the carrier
sheet.

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1 The thermoformable laminate 70 illustrated in FIG.
7 also can be formed by separate laminating steps, each
similar to the laminating step illustrated in FIG. 6.
In this embodiment, a separate color coat is first
5 transferred from a casting sheet to the backing sheet.
The color coat may have a size coat to bond the color
coat to the backing sheet. The casting sheet is
stripped away after laminating. The dried clear coat is
then transferred from a separate casting sheet to the
10 face of the color coat opposite from the backing sheet.
No size coat is necessary to bond the clear coat to the
color coat during the hot laminating step.

Thermoforming

15 In the next step in the process, the laminate 70
shown in FIG. 7 is thermoformed into a desired three-
dimensional shape. FIGS. 8 and 9 illustrate one example
of a thermoforming step in which the initially flat
laminate can be formed into a highly contoured three-
20 dimensional shape for use as the surface of a car body
panel. Referring to FIGS. 8 and 9, separate laminate
sheets are individually placed inside a clamping frame
106 of a vacuum-forming machine. The clamping frame is
movable back and forth on a track 108. The laminate
25 sheet is initially placed in the clamping frame at the
position shown in phantom lines at 106 in FIG. 8.

The clamping frame is then moved along the track
into an oven 110 for heating the back sheet to a
thermoforming temperature. An ABS backing sheet is
30 heated to a temperature in the range of about 280° to
about 380°F, and for Bexloy nylon the sheet is heated to
a temperature from about 380° to about 420°F. These
temperatures are actual sheet temperatures, not oven
temperatures. The actual thermoforming temperatures
35 used, within these ranges, may be a factor in preventing

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1 deglossing of the clear coat during thermoforming. In
some instances described in the examples below, a lower
thermoforming temperature can prevent deglossing or
formation of small cracks in the surface of the paint
5 coat. These phenomena may otherwise occur at higher
thermoforming temperatures. A pressure assist can be
used with the thermoforming step in order to reduce the
thermoforming temperature. A lower thermoforming
temperature of about 270°F may assist in producing
10 higher gloss and distinctiveness-of-image in the
finished surface. At thermoforming temperatures the
laminate 70 sags as shown at phantom lines at the right
side of FIG. 8.

After the laminate is heated in the oven 110 to the
15 desired temperature, the clamping frame is moved back
along the track, away from the oven 110 to its original
position above a vacuum-forming buck 112. The working
surface of the vacuum-forming buck 112 is shown in FIGS.
8 and 9 as a curved surface, by way of example only.
20 Other configurations can be used depending upon the
desired three-dimensional shape imparted to the surface
of the finished article.

The preheated laminate is next vacuum-formed into
the desired three-dimensional shape by first drawing a
25 vacuum on the vacuum-forming buck 112 through its
connection 114 to a vacuum pump. The vacuum-forming
buck 112 is then raised to the position shown in FIG. 9,
where it has risen into the clamping frame. The vacuum
is pulled through holes in the buck to force the molten
30 plastic into the shape of the working surface of the
buck. Positive air pressure can be applied to the free
face of the clear coat on the opposite side of the back
to increase forming pressure. The buck stays in place
long enough to cool the plastic to a solid state again
35 before the buck drops away back to the position shown in

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1 FIG. 8. This leaves behind the plastic in the shape of
the buck. The preferred vacuum-forming step is to use a
male vacuum former in which the vacuum-forming buck 112
is in direct contact with the backing sheet so as to not
5 contact the exterior clear coat 45 on the opposite side
of the backing sheet. In this way, the backing sheet
hides most of any of the possible defects in the working
surface of the buck; and the surface of the clear coat
is not affected, but is allowed to elongate freely.

10 In an alternate thermoforming step (not shown), the
laminate 70 can be fed to the thermoformer as a
continuous sheet. The laminate first passes through the
oven and then passes to the thermoforming buck in line
with the downstream end of the oven. The continuous
15 sheet is stopped at preset intervals for heating the
laminate to the thermoforming temperature while a
previously heated portion of the sheet is vacuum formed
into the desired shape.

The thermoforming step produces a three-
20 dimensionally shaped preformed laminate 116 illustrated
in FIGS. 10 and 11. For simplicity, the preformed
laminate is illustrated as comprising the backing sheet
72 and the composite paint coat 44 adhered to it. The
laminate is illustrated in a three-dimensionally shaped
25 form following the thermoforming step as one example
only of a possible three-dimensional shape. Other
complex three-dimensional shapes are also possible. The
composite paint coat resists elongation greater than
about 40% during thermoforming without deglossing,
30 cracking, stress-whitening, or otherwise appreciably
disrupting the exterior automotive durability and
appearance properties that were present in the composite
paint coat before thermoforming.

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1 Bonding of Thermoformed Laminate to Substrate Panel

FIGS. 10 and 11 schematically illustrate steps in a subsequent injection-cladding operation in which the preformed laminate 116 is adhered to an underlying plastic substrate panel. The injection-cladding step is an example of a possible means for adhering the laminate to the substrate. Following the thermoforming step, the laminate is placed in an injection mold 117 and fused to the face of an injection-molded substrate 118. FIG. 10 illustrates a first step in the injection-cladding step in which a plastic injection mold is in its open position, and the preformed laminate 116 is placed in the mold cavity between front and rear mold halves 120 and 122. The inside surface 124 of the mold half 120 identically matches the exterior contour of the paint-coated surface of the preformed laminate. This surface 124 of the mold is a rigid, high gloss, highly-polished surface which is free of surface defects so that surface defects are not transferred to the high gloss, clear-coated surface of the laminate. After the laminate is preformed to its desired shape, it is trimmed to size and is ready for injection-cladding. The vacuum-formed die cut sheet is placed inside the injection mold and the mold halves 120 and 122 are closed, leaving a space of the desired size behind the laminate for receiving the injection molding material. As shown best in FIG. 11, the injection molding material 118 flows through a passage 126 in the rear mold half 122 and into the mold cavity behind the preformed laminate 116. The molding material conforms to the shape of the mold cavity and is permanently fused to the backing sheet portion of the laminate. The injection molding material does not come into contact with the paint coat. As described previously, the molding materials from which the substrate 118 and the backing sheet 72 are made are

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1 compatible so that the two materials fuse to form an
integral molded substrate on which the paint coat
provides a defect-free finish. The temperature at which
the injection-mold is operated is substantially below
5 the melt temperature of the molding material. In one
embodiment, in which an ABS backing sheet is used, the
molten material is at a temperature of about 450°F, for
example. A water jacket can be used to cool the faces
of the mold. During injection-molding, the backing
10 sheet material softens when fusing to the injection
molding material, and the surface of the clear coat
replicates the surface of the mold, owing to the
pressure from the molding operation. Both faces of the
mold are cooled to a temperature in the range of about
15 160° to 170°F, so that the paint coat 44 on the laminate
remains stable during injection molding. The clear coat
material at the time of injection molding has had all of
its solvent gas removed so that evolution of gases
during injection molding is essentially avoided. As a
20 result, the clear coat retains its high gloss surface
characteristics during the injection molding step.

FIG. 12 schematically illustrates the finished
article 130 produced by the process of this invention.
In the finished article, the preformed laminate and its
25 backing sheet have been fused to the molded substrate
118. In one embodiment, the article can be an exterior
car body member or panel. The exterior clear coat 45
and the color coat 46 combine to produce a paint coat
with exterior automotive properties on the surface of
30 the substrate. Any defects in the substrate material
have been absorbed by the 20 mil thick backing sheet 72
to provide a defect-free paint coat.

Alternatively, the color coat may in some instances
be eliminated or the pigmentation reduced, and the
35 coloration may be provided by pigments contained in the

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1 backing sheet or molding material for the substrate. In
these instances, the clear coat is used with the backing
sheet which is thermoformed and then adhered to the
substrate according to the processing techniques
5 described previously. As one advantage, coloration
contained in the backing sheet can hide the effects of
chipping of the paint coat.

Although the invention has been described with
respect to the injection-molding steps illustrated in
10 FIGS. 10 and 11, other techniques can be used for
forming the finished article illustrated in FIG. 12.
These include, but are not limited to, use of sheet
molding compound (SMC), compression cladding and
reaction injection molding (RIM) techniques, and
15 pressure-sensitive or adhesive bonding techniques.
Other plastic molding materials also can be used in
place of ABS for fusing the substrate panel to the
paint-coated backing sheet. These may include thermo-
plastic polyolefins (TPO's) such as polypropylenes and
20 polyethylenes; polyesters; and amorphous nylon. In
these instances, the backing sheet is preferably made
from the same polymeric material as the injection
molding material.

25 Characteristics of Finished Paint Coat

The following is a list of physical properties
which are used herein to measure whether the finished
paint coat is useful as an exterior automotive paint
coat:

- 30 (1) Gloss
- (2) Distinctiveness-of-Image
- (3) Color Uniformity (hiding ability)
- (4) Dry Film Thickness Uniformity
- (5) Gasoline Resistance
- 35 (6) Solvent Resistance

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- 1 (7) Acid Spotting Resistance
- (8) Hardness
- (9) Abrasion Resistance
- (10) Impact Strength
- 5 (11) Adhesion of Paint Coat
- (12) Accelerated UV Resistance
- (13) Resistance to Water and Humidity Exposure

10 Properties (1) through (4) are considered appearance properties and properties (5) through (13) are considered durability properties. Specifications and test methods for each of these physical properties are described below. Certain specifications and test methods identified below are defined by publicly available standard industry specifications and test methods which are incorporated herein by this reference.

15 (1) Gloss is measured by specular reflectance of a beam of light at angles of 20° and 60°. The desired specular reflectance for an exterior automotive paint coat surface is at least about 60 to 65 gloss units at 20°, and at least about 75 to 80 gloss units at 60°. Specular reflectance and other criteria herein are measured before the finished painted surface is buffed and waxed. A preferred test method is described in GM Test Specification TM-204-A. The Byk-Mallinckrodt "multigloss" or "single gloss" gloss meters can be used for measuring specular gloss of the finished surface. These gloss meters give values equivalent to those obtained from ASTM Method D-523-67. Either gloss meter is used with gloss standards covering the expected range of measurement, together with a piece of polished black glass plate of known refractive index. The gloss meter is calibrated by setting it to read the gloss of a highly polished standard and then reading the gloss of a working standard having a value preferably in the range

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1 of the test panel. The second standard should agree
within one unit of its assigned value. At least two
readings are taken on a different area of the test
panel. These values are averaged if they agree within
5 one unit. If the range is larger than one unit,
additional regions are taken and a mean value is
calculated.

(2) Distinctiveness-of-Image (DOI) is a
measurement of the clarity of an image reflected by the
10 finished surface. DOI can be measured from the angle of
reflection of a light beam from a spherical surface.
The desired DOI for an exterior automotive paint coat
surface is at least about 60 units, where 100 units is
the maximum DOI reading. DOI is measured by the
15 Hunterlab Model No. D47R-6F Dorigon Gloss Meter. A test
panel is placed on the instrument sensor and the
sharpness of the reflected image is measured. Details
of the DOI test procedure are described in GM Test
Specification TM-204-M, which are incorporated herein by
20 reference.

(3) Color Uniformity is a test to determine
whether coloration of the paint coat remains uniform
after thermoforming and injection-cladding. Coloration
is tested after the paint coat is coated on the casting
25 sheet, before transfer to the backing sheet. Coloration
testing is repeated after a deep draw stretch simulating
elongation during thermoforming, to determine whether
the color has changed. A desirable coloration
uniformity can be a color change of no greater than
30 about one to two McAdam units on a colorimeter.

(4) Dry Film Thickness (DFT) is a standard
industry measurement of the film thickness of the
finished paint coat, to determine whether the paint coat
thickness matches a required film thickness specified by
35 the auto manufacturer. For the present exterior

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1 automotive specifications, uniformity of the finished
paint coat is determined to be a more useful parameter
in determining whether the paint coat meets appearance
requirements. Thickness uniformity of the finished
5 paint coat can be measured from several locations on the
finished article, including highly contoured areas, to
determine whether variations in the thickness of the
finished paint coat exceed a desired level.

(5) Gasoline Resistance requires no color change,
10 degradation, tackiness, marring or loss of paint
adhesion on plastic parts used on and adjacent to fuel
filler openings after being immersed for ten seconds,
ten times, in a specified reference fuel with a 20
second dry off period between each immersion.
15 Immediately after the tenth immersion, the painted
surface is checked and must pass Thumbnail Hardness
according to GM Test Specification TM 55-6, incorporated
herein by reference..

(6) Cleanability is tested according to GM Test
20 Specification TM 31-11 which is incorporated herein by
reference. According to this test, the painted plastic
part is required to withstand ten rubs with cheesecloth
saturated with 9981062 Naphtha or currently used and
approved cleaning solvents, with no evidence of
25 staining, discoloration, or softening of the painted
surface. This test requires no evidence of color
transfer from the test part to the cloth. One rub
consists of one forward and backward motion.

(7) Acid Spotting Resistance requires the test
30 part to withstand exposure to 0.1 N sulfuric acid for 16
hours without any evidence of staining, discoloration,
or softening of the painted surface.

(8) Hardness is measured by a standard Knoop
Hardness Test. The required hardness is at least a
35 Knoop hardness number of four.

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1 (9) Abrasion Resistance is tested by a
gravelometer under the standard test method identified
as SAE J-400. According to this test, the painted part
shall withstand the Gravelometer Test at minus 10°F with
5 a minimum rating of eight (F.B. Gravelometer Rating
Chart). The tested part should withstand the
Gravelometer Test as-received and after Florida exposure
described below. A Fisher Body Material Specification
FBMS 26-7 (incorporated herein by reference) also
10 defines a minimum level of wear resistance for the
finished paint coat.

 (10) Impact Strength is tested at room temperature
by the Gardener Test and by the Rosand Test at minus
20°F. The paint coat should withstand at least 20 inch-
15 pounds of direct impact with no failure.

 (11) Paint Adhesion is tested by a standard Tape
Adhesion Test described in GM Test Specification TM
55-3, which is incorporated herein by reference.
According to this test, a tape is pressed down over an
20 X-shaped cut in the paint coat and the tape is then
removed to test the amount of peeling. The Adhesion
Test requires a minimum of 99% of the paint remaining in
the tape test area.

 (12) Accelerated UV Resistance, also referred to as
25 Accelerated Weathering, or QUV, measures the
weatherability of a paint coat in accelerated test
procedures designed to provide an accurate indication of
long-term UV resistance or other weatherability
properties. According to a QUV test useful for
30 measuring accelerated UV Resistance, the test panel
should not show any significant surface deterioration or
embrittlement, loss of coating adhesion, objectionable
shrinkage, or noticeable color or gloss change after
about 500 to 1,000 hours exposure to UV light and

35

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1 condensation apparatus per ASTM G-53 using eight hour UV
cycle at 70°C and four hour humidity cycle at 50°C.

(13) Resistance to Water and Humidity Exposure is
measured by several tests. According to a first test,
5 the finished part shall withstand 96 hours of humidity
exposure at 100% relative humidity and 100°F in a
humidity cabinet defined in GM test specification TM 55-
3, and a two-hour water immersion test at 100°F accord-
ing to GM test specification TM 55-12. These test
10 specifications are incorporated herein by reference.
The resulting test panel should show no evidence of
blistering when examined one minute after removal from
the test cabinet and shall withstand the Paint Adhesion
Test described above. The Paint Adhesion Test is
15 performed within one minute after removal from either
test cabinet. In a second test, the finished part
should withstand 15 cycles of the Moisture-Cold Cycle
Test defined in GM test specification TM 45-61A
(incorporated herein by reference), without any visible
20 signs of cracking or blistering. After 15 cycles, the
part shall withstand 96 hours of the humidity exposure
described above, followed by passing the Paint Adhesion
Test also described above. The Paint Adhesion Test is
performed within one minute after removal from the
25 humidity environment. One cycle consists of 24 hours
and 100% relative humidity at 100°F, 20 hours at minus
10°F, and four hours at room temperature.

Other durability tests can be used to determine the
usefulness of a paint coat for exterior automotive
30 applications. These tests can include long-term ultra-
violet radiation exposure and heat exposure tests. Both
of these tests require long-term exposure of the panel
to the particular environment. For instance, one long-
term UV test can require two years exposure to determine
35 the long-term resistance of the paint coat to

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1 ultraviolet radiation. In a long-term weathering and
heat resistance test, the painted plastic part is
required to withstand two years direct Florida and
Arizona test site exposure without any significant color
5 or gloss change, loss of adhesion, or other detrimental
surface or substrate deterioration effects. After long-
term Florida and/or Arizona exposure, painted samples
must withstand testing under the Tape Adhesion,
Abrasion, Gravelometer and Moisture-Cold Crack Cycling
10 tests. Five years Florida and Arizona test site
exposure also can be used. Other test methods can
include sulfide staining, detergent resistance, solvent
resistance, compatibility, cycle tests, humidity and
adhesion, humidity and wear resistance, cold exposure,
15 and Florida and Arizona exposure tests set forth in FBMS
26-7.

Example 1

A high gloss jet black laminated exterior
20 automotive paint coat was formed on the exterior surface
of an experimental plastic rear window molding for a
Pontiac Grand AM. The window molding was similar to
that shown in FIG. 2. The paint coat was first coated
onto a surface of a flexible polyester film casting
25 sheet. The flexible carrier comprised two mil thick
high gloss American Hoechst 3000 polyester film. The
paint coat comprised a clear coat, a color coat, and a
size coat coated onto the polyester film casting sheet
in that order. A thin film of wax was first coated on
30 the polyester film. The wax coating formulation
comprised, on a weight basis, 40% xylene, 59.4%
cyclohexanone, and 0.6% carnauba wax. The wax was
dissolved in the solvents at 120°F and cast on the
polyester film using a gravure coating cylinder. The
35 wax coating was applied as a thin film approximately

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1 0.001 mil thick. The wax-coated casting sheet was then
passed through a drying oven and dried at 250°F with a
line speed of 25 feet per minute. The wax-coated
5 casting sheet could be separately run at a higher lineal
speed, if desired. The wax film did not affect
replication of the polyester film surface by the clear
coat.

The clear coat was then prepared from the following
formulation:

10	<u>Ingredient</u>	<u>Parts</u>
	BLO (Butyrolactone)	15.00
	DIBK (di-isobutyl ketone)	27.00
	Polymethyl methacrylate (Elvacite 2010)	18.00
15	PVDF (Kynar 301F)	18.00
	BLO	6.28
	Cyclohexanone	15.00
	Silicone fluid (Dow Corning DC-11)	0.72

20 The Elvacite 2010 acrylic resin was mixed with the
BLO and DIBK solvents under heat applied at
approximately 130°F to dissolve the acrylic resin in the
solvents. The resulting mixture was then allowed to
cool over night. The PVDF, together with the remainder
25 of the BLO and cyclohexanone solvents and the silicone
fluid, were then mixed at room temperatures so that the
PVDF component remained as a dispersion in the mixture,
rather than dissolving. The dried clear coat contained
approximately 50% PVDF and 50% polymethyl methacrylate,
30 by weight, based on the total PVDF-acrylic solids.

The clear coat was coated on the casting sheet in a
dry film thickness of about 0.8 mil. The clear coat was
applied to the sheet by a reverse roll coater
(illustrated in FIG. 5) in line with the gravure oven
35 previously used for drying the wax film, so that the

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1 clear coat was applied directly after drying of the wax.
The clear coat was dried on the carrier sheet by passing
it through a multi-zone impinging air drying oven having
three heating zones spaced apart axially along the
5 length of the carrier, with each drying zone having a
progressively higher temperature. The clear-coated
carrier was passed through the heating zones at a line
speed of 25 feet per minute and each heating zone was 40
feet long. Temperatures of the three heating zones
10 were: Zone 1: 260°F, Zone 2: 330°F, Zone 3: 390°F.
Passing the clear coat through the three heating zones
removed substantially all solvent gases from the clear
coat to produce a dry clear coat of uniform film
thickness.

15 A jet black color coat was next coated on the dried
clear coat at a dry film thickness of about 0.8 mil.
The color coat formulation was as follows:

	<u>Ingredient</u>	<u>Parts</u>
	Cyclohexanone	9.27
20	DIBK	18.54
	BLO	8.34
	Polyethyl methacrylate (Elvacite 2042)	10.02
	Dispersing agent (Solsperse 17,000)	0.10
25	PVDF (Kynar 301F)	24.04
	BLO	14.14
	Black Dispersion	15.00

30 The black dispersion comprised carbon black in a
vehicle of Elvacite 2043, available commercially as
Gibraltar 438-39110 pigment. The color coat formulation
was prepared in a similar manner to the clear coat
formulation in that the acrylic resin was first
dissolved in the cyclohexanone, DIBK and BLO solvents at
35 a temperature of about 130°F and was then allowed to

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1 cool before the PVDF component was added to the mixture
to form a dispersion of the PVDF in the acrylic resin.
The pigment was then added to the resulting mixture to
produce a jet black color. On a weight basis, the
5 amount of pigment contained in the color coat
formulation was about 4% to about 5%. The dried color
coat comprised approximately 65% PVDF and approximately
35% acrylic resin, by weight of the total PVDF and
acrylic (non-pigment) solids. The acrylic resin
10 component comprised polyethyl methacrylate comprised of
approximately 90% Elvacite 2042 and approximately 10%
Elvacite 2043. The color coat was coated onto the dried
clear coat in liquid form and then passed through the
three stage oven described above to dry the color coat.
15 A size coat was next prepared for use with an ABS
backing sheet. The size coat comprised 50 parts methyl
methacrylate resin known as Acryloid A-101 (a trademark
of Rohm and Haas Co.) dissolved in 50 parts methyl-
ethyl-ketone solvent. The size coat was coated onto the
20 dried color coat in a dry film thickness of about 0.1
mil using a single station gravure coating cylinder.
The size coat was then dried by passing it through a
single stage drying oven at a temperature of about
275°F.

25 The resulting paint-coated carrier was then passed
to a laminating operation similar to that illustrated in
FIG. 6, where the paint coat was transferred from the
polyester carrier to a 20 mil thick ABS backing sheet.
In the laminating operation, the backing sheet and the
30 paint-coated carrier were run at a lineal speed of 15
feet per minute, and the laminating drum was operated at
a temperature of 400°F. The size coat was heat-acti-
vated and the paint coat was transferred from the
carrier to the face of the ABS backing sheet during the
35 laminating operation, in which the hot steel drum

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1 applied a force of about 300 pounds per lineal inch.
The polyester carrier film was stripped away from the
surface of the laminate, leaving the paint coat bonded
to the ABS sheet, with the clear coat providing a high
5 gloss surface on the exterior of the ABS backing sheet.

The paint-coated laminate was then thermoformed
into a complex three-dimensional shape to form the
plastic window molding. The laminate was thermoformed
by first heating the flat laminate in an oven to a
10 temperature of about 360°F, to soften the laminate.
After the laminate was heated, it was placed over a
vacuum-former buck similar to that shown in FIGS. 8 and
9, and a vacuum was drawn against the buck on the ABS
side of the laminate to form the heated laminate into
15 the three-dimensional shape of the window molding.

The thermoformed laminate was then trimmed to fit
in the mold cavity of a plastic injection molding
machine. An ABS plastic molding material, for forming
the substrate base of the window molding, was injected
20 into the mold behind the thermoformed laminate to fuse
the ABS molding material to the laminate. The mold was
operated at normal melt temperature for the ABS resin.
This formed a window molding as a integral plastic part
with a defect-free, paint coat on the exterior surface
25 of the panel.

The window panel was tested and the tests
demonstrated the usefulness of the paint coat as an
exterior automotive paint coat. The test results
indicated that desirable appearance properties,
30 including gloss, were produced. Gloss measured 62 units
at 20° and 79 units at 60°. DOI measured 64. Color
uniformity was good. The test results also demonstrated
a desirable combination of durability properties. The
test panel passed gasoline resistance, acid resistance,
35 abrasion resistance (gravelometer reading of 8), impact

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1 resistance (80 in-lb. for Gardner Test), QUV, and 96-
hour humidity exposure tests, according to test methods
similar to those described above.

5 Example 2

A high gloss red laminated exterior automotive
paint coat was formed on the exterior surface of a
highly contoured plastic automobile body panel. The
lamine was matched to a General Motors Fiero red body
color and used to make a prototype injection-clad Fiero
rear quarter panel. The paint coat was first coated
onto a casting film comprising a two mil thick high
gloss American Hoechst 3000 polyester film. A clear
coat, color coat, and size coat were coated onto the
casting film in that order. The clear coat was prepared
from the following formulation:

	<u>Ingredient</u>	<u>Parts</u>
	Cyclohexanone	15.47
	BLO (Butyrolactone)	7.52
20	DIBK (di-isobutyl ketone)	21.66
	Polyethyl methacrylate (Elvacite 2042)	12.95
	UV absorbers	1.1
	PVDF (Kynar 301F)	24.05
25	BLO	17.24

The Elvacite acrylic resin was dissolved in the
BLO, DIBK and cyclohexanone solvents, while mixing and
under heat at approximately 130°F. The resulting
mixture was allowed to cool overnight. The UV absorbers
were then added to the mixture and the PVDF was
dispersed in the resin. The remaining BLO solvent was
added to dilute the final mixture. The PVDF component
remained as a dispersion in the mixture rather than
dissolving. The dried clear coat contained approxi-

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1 mately 65% PVDF and 35% acrylic resin, based on the
total PVDF and acrylic solids.

2 The clear coat was coated on the casting film in a
dry film thickness of 0.6 mil. The wax coat described
5 in Example 1 was omitted in this test. The clear coat
was dried on the casting sheet by passing it through the
same three-zone drying oven described in Example 1.
Line speed and temperatures of the three zones were the
same. Passing the clear coat through the drying oven
10 removed substantially all solvent gases from the clear
coat and produced a dry clear coat of uniform film
thickness.

A red color coat was next coated on the dried clear
coat at a film thickness of about 0.8 mil. The color
15 coat formulation was as follows:

	<u>Ingredient</u>	<u>Parts</u>
	Cyclohexanone	10.61
	Polyethyl methacrylate (Elvacite 2042)	2.99
20	Dispersing agent (Solsperse 17,000)	0.10
	PVDF (Kynar 301F)	19.95
	BLO	4.02
	Solvent (M-Pyrol)	8.45
25	Red Dispersion	57.9

The dispersion comprised several pigments as a
powder mixed in a vehicle comprising polyethyl
methacrylate resin, Elvacite 2043, 16% solids, and 84%
30 cyclohexanone solvent. The color coat formulation was
prepared in a similar manner to the clear coat
formulation, in that the acrylic resin was first
dissolved in the solvents at a temperature of about
130°F. The dispersing agent and a portion of the red
35 dispersion were added. The mixture was allowed to cool

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1 to room temperature and the PVDF component was dispersed
using a high speed mixer. The remainder of the red
dispersion was then added to the resulting mixture to
produce a red color match. The dried color coat
5 comprised approximately 65% PVDF and approximately 35%
acrylic resin, by weight of the total PVDF and acrylic
(non-pigment) solids. The acrylic resin component com-
prised polyethyl methacrylate, approximately 80%
Elvacite 2043 and approximately 20% Elvacite 2042. The
10 pigment was present in a ratio of three parts pigment to
ten parts resin binder, or approximately 23% of the
total solids. The color coat was coated onto the dried
clear coat in liquid form and then passed through the
three-stage oven described above for drying the color
15 coat.

A size coat was next prepared for use with an ABS
backing sheet. The size coat comprised 75 parts methyl
methacrylate resin, Acryloid A-101, dissolved in 25
parts toluene solvent and mixed until homogeneous. (The
20 Acryloid A-101 comprised 40% PMMA solids in MEK
solvent.) The size coat was then coated onto the dried
color coat in a film thickness of about 0.1 mil. The
size coat was applied by a reverse roll coater similar
to that described in FIG. 5 and was then dried in the
25 same three-stage drying oven as the clear coat and the
color coat. The resulting paint-coated carrier was
transferred to a laminating operation similar to that
illustrated in FIG. 6, where the paint coat was
transferred from the polyester carrier to a 20 mil thick
30 ABS backing sheet. The carrier film was stripped away
from the surface of the laminate, leaving the red paint
coat with a high gloss surface on the exterior of the
ABS backing sheet.

The laminate was then thermoformed into the complex
35 three-dimensional shape of the rear quarter panel. The

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1 laminate was thermoformed by passing it, as a continuous
sheet, through an oven for heating the laminate to a
temperature of about 290°F. After the continuous sheet
was heated to this temperature, it was then moved over a
5 vacuum-former and a vacuum was drawn to form the
laminate into the three-dimensional shape of the rear
quarter panel. Positive air pressure of 15 psi was
applied to the clear-coated free face of the sheet and
the vacuum was drawn on the ABS side of the sheet.

10 The thermoformed laminate was placed in the mold
cavity of a plastic injection mold, and an ABS-based
plastic molding material for forming the substrate base
of the quarter panel was injected into the mold behind
the thermoformed laminate, to fuse the molding material
15 to the ABS side of the laminate. This formed the rear
quarter panel as an integral plastic part with a defect-
free, glossy paint coat on the exterior surface of the
panel.

20 The panel was tested, and the tests demonstrated
the usefulness of the paint coat as an exterior
automotive paint coat. The test results indicated that
desirable appearance properties, including gloss, were
produced. Gloss measured 65 units at 20° and 80 units
at 60°. DOI measured 65. Color uniformity was good.
25 The test results also demonstrated a desirable
combination of durability properties. The test panel
passed gasoline resistance, cleanability, acid
resistance, hardness (7-8 reading on Knoop hardness
scale), abrasion resistance (gravelometer reading of 8),
30 impact resistance (80 in-lb. for Gardner Test), QUV, and
96-hour humidity exposure tests, according to test
methods similar to those described above. Florida
exposure passed after three months.

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1 Example 3

 Tests were conducted to determine the relative proportions of the PVDF and acrylic components of the clear coat and the color coat capable of producing a composite paint coat that can be cast as a film, laminated to a backing sheet, thermoformed, and injection-clad to form a finished article with an exterior automotive paint coat surface. In this example, standard spray type automotive acrylic enamel paints manufactured by DuPont were used as a paint coat in the process of this invention. These types of paint systems are commonly used at present as exterior automotive paint. The paint coats were thermoset and they cross-linked at low temperatures on the carrier when dried. These paint coats were then transferred from the carrier to a 20 mil thick ABS backing sheet which was then drawn on a vacuum-former. The paint coat was too brittle to elongate properly; it cracked and shattered at stress points in the laminate when thermoformed.

 Similar DuPont urethane-based automotive paints normally used on rubber bumpers also failed in a similar manner when thermoformed. These paint systems were stable at room temperature but they cracked during high temperature vacuum-forming.

25 Example 4

 In a test similar to that described in Example 3, a non-thermoset acrylic lacquer paint coat was evaluated. The paint coat comprised a DuPont lucite dispersion lacquer thermoplastic acrylic resin paint system. The paint coat was coated on a casting sheet, dried, and laminated to a 20 mil thick ABS backing sheet. This paint system could be thermoformed, but it was difficult to process. If used as a high-solids (low solvent)

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1 paint coat, the lacquer took too long to dry. If
stabilizers were added to improve drying, it cracked
when thermoformed. It also tended to adhere to the
injection mold.

5

Example 5

Other pure thermoplastic acrylic resin paint
systems were tested, such as a polymethyl methacrylate
and solvent-based paint coat with dispersed pigments.
10 Such pure acrylic paint systems were characterized
primarily by their difficulty in processing because of
their slow rate of solvent evaporation during drying and
a tendency to adhere to the surface of the injection
mold. Acrylic paint systems with appreciable amounts of
15 pigment deglossed during thermoforming. Pure
thermoplastic acrylic paint systems also tended to lack
certain mechanical properties that did not meet exterior
automotive criteria, including low abrasion resistance
(gravelometer) properties. In addition, these pure
20 acrylic resin formulations did not cast well in film
form because of their tendency to adhere too strongly to
the casting sheet.

Example 6

25 A pure PVDF (Kynar 301F) paint system was tested in
the process of this invention. The PVDF paint system
had sufficient elongation to thermoform properly without
cracking, but it deglossed excessively during
thermoforming.

30

Example 7

A thermoplastic acrylic-vinyl paint system was
tested experimentally according to the process of this
invention. The paint system also included a dispersed
35 black pigment, about 3% by weight of the total solids.

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1 This paint system had been used successfully previously
for interior automotive trim parts on dashboard panels
and the like. The paint system could be laminated to an
5 ABS backing sheet, but when it was thermoformed, it
deglossed excessively. This interior paint system did
not produce an exterior automotive paint surface that
meets minimal gloss and DOI specifications for exterior
automotive use. This paint coat, when used for auto-
10 motive interior parts, also is not applied with a film
thickness necessary to meet durability specifications
for an exterior automotive finish. Using the higher
level of pigment required for an exterior automotive
paint coat produced extreme deglossing during thermo-
forming. Other mechanical properties necessary for
15 exterior use also were not present.

Example 8

A blended thermoplastic PVDF-acrylic paint system
was tested experimentally with the process of this
20 invention. This blended paint system comprised a
dispersion of 72% PVDF and 28% acrylic resin, by weight
of the total PVDF-acrylic solids. This paint system was
similar to one used commercially on exterior metal trim
parts for automobiles in which the metal was spray
25 painted and then cold-formed to produce the desired trim
part. This blended paint system contained a dispersion
of black pigment comprising about 3% by weight of the
total solids. This paint system was not suitable for
exterior automotive use. The paint system could be
30 laminated to an ABS backing sheet, but when
thermoformed, it deglossed excessively. In addition to
its low gloss, this paint system also did not possess
the exterior DOI requirements for an exterior automotive
finish.

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1 Example 9

 A PVDF and acrylic resin clear coat was tested in combination with a pure acrylic-based color coat. Each paint coat was coated on a casting sheet, the coatings were dried and transferred to an ABS backing sheet to form a composite paint coat, and the sheet was thermoformed. In one test, the acrylic resin component in the color coat comprised an outdoor weatherable acrylate known as Korad D, a product of Polymer Extruded Products of Newark, New Jersey. Other tests were conducted with pure acrylic color coat formulations comprising PMMA and PEMA copolymers. In one test, the color coat comprised a pure Elvacite 2042 polyethyl methacrylate. Visual observation of the thermoformed laminates indicated that good appearance properties, including gloss and DOI, were achieved. One observation was that a PVDF and acrylic clear coat can be used in combination with a color coat not containing the PVDF component, resulting in a less expensive composite paint coat that eliminates the more expensive fluorocarbon component from a portion of the finished paint coat.

Example 10

 Tests were conducted on a composite paint coat comprising an exterior clear coat bonded to a color coat. The solids in the clear coat and the color coat both consisted essentially of a blended thermoplastic PVDF-acrylic paint system. The paint coat was coated on a casting sheet, transferred to an ABS backing sheet, thermoformed, and injection-clad to an ABS substrate. It was determined that certain PVDF/acrylic ratios in the clear coat did not produce a sufficient combination of the appearance and durability properties in the finished laminate suitable for exterior automotive use. For instance, 100% PVDF deglossed during thermoforming,

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1 whereas 100% acrylic resin created processing problems,
including adherence to the injection mold and slow
solvent evaporation. FIG. 13 shows a graph representing
a performance curve for the PVDF-acrylic based composite
5 paint coat. This curve represents the relationship
between gloss (gloss units at 60°) of the clear coat on
the finished article and the ratio of PVDF to acrylic in
the dried clear coat, by weight of the total PVDF and
acrylic-based solids. This curve is based upon
10 experimental evaluations of clear coat formulations
comprising PVDF and various acrylic resin combinations,
primarily combinations of polymethyl methacrylate and
polyethyl methacrylate, or mixtures thereof, including a
range of low to very high molecular weight acrylic
15 resins. This curve illustrates that a transition point
exists between acceptable gloss and unacceptable
deglossing above about 65% to 70% PVDF in the clear coat
formulation. If the PVDF is contained in a formulation
greater than about 70%, excessive deglossing is produced
20 upon thermoforming. The tests used to determine the
performance curve also revealed that a 50/50 ratio of
PVDF to acrylic is approximately where addition of a
greater proportion acrylic resin makes processing of the
paint system too difficult. The lined portion of the
25 curve represents a workable combination of PVDF and
acrylic resin, for these particular resin combinations,
to produce a clear coat having a desirable gloss level.
The minimum desired gloss level, for the purpose of this
example, was selected as 75 units for 60° specular
30 reflectance. These tests have shown that polymethyl
methacrylate in the PVDF and acrylic paint system can
produce a generally higher gloss level than polyethyl
methacrylate; and therefore, the curve illustrated in
FIG. 13 will tend to rise as proportionately more
35 polymethyl methacrylate is used. The curve will become

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1 lower as more polyethyl methacrylate is used. Moreover,
the tests have shown that addition of pigment to the
underlying color coat may cause greater deglossing of
the exterior clear coat during thermoforming; and there-
5 fore, the curve illustrated in FIG. 13 will tend to
become lowered as the pigment level in the color coat
increases. Tests have also shown that deglossing of the
clear coat may be caused by several factors. For
instance, if the clear coat is too thin, the pigment
10 particles from the underlying color coat may migrate
through the surface of the clear coat upon thermoforming
and cause at least some deglossing. In certain
instances, a thicker clear coat can resist this type of
deglossing. However, in other instances, a thicker
15 clear coat does not prevent deglossing. In one test, a
relatively thick (1.2 mil) clear coat comprising 50%
PVDF and 50% polymethyl methacrylate deglossed when
thermoformed at 340°F. The underlying color coat
contained a substantial pigment level of 23%. By
20 increasing the PVDF in the clear coat to 65% solids and
by changing the acrylic component to 35% polyethyl meth-
acrylate, and by using a lower thermoforming temperature
of 290°F., deglossing of the clear coat was prevented.

25 Example 11

Experiments were conducted to compare the physical
properties of exterior automotive PVDF/acrylic coatings
prepared as a solution of PVDF in the acrylic resin with
similar dispersion systems. The tests were conducted
30 for both the clear coat and the color coat to compare
gloss and distinctiveness-of-image (DOI) levels for
thermoformed panels made with combinations of both
solution and dispersion cast PVDF/acrylic films.
Dispersion and solution clear coats and color coats were
35 produced from the following formulations:

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1 Dispersion clear coat:

	<u>Ingredient</u>	<u>Parts</u>
	Polymethyl methacrylate (Elvacite 2010)	50
5	PVDF (Kynar 301F)	50
	High boiling point acetate solvent (Exxate 700)	74
	Solvent (M-Pyrol)	55.5
	Cyclohexanone	55.5

10 Solution clear coat:

	<u>Ingredient</u>	<u>Parts</u>
	Polymethyl methacrylate (Elvacite 2010)	50
	PVDF (Kynar 301F)	50
15	Solvent (M-Pyrol)	225
	Methethylketone	225

Dispersion color coat:

	<u>Ingredient</u>	<u>Parts</u>
20	DIBK (di-isobutyl ketone)	18.55
	BLO (Buytrolactone)	8.34
	Polyethyl methacrylate (Elvacite 2042)	10.20
	Cyclohexanone	9.27
25	Dispersing agent (Solsperse 17,000)	0.10
	PVDF (Kynar 301F)	24.40
	BLO	14.14
	Black dispersion	15

30

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1 Solution color coat:

	<u>Ingredient</u>	<u>Parts</u>
	Polyethyl methacrylate (Elvacite 2042)	10.20
5	Dispersing agent (Solsperse 17,000)	0.10
	PVDF (Kynar 301F)	24.40
	Black dispersion	15.00
	Solvent (M-Pyrol)	86.00
10	Methylethylketone	74.30

15 The dispersion clear coat was prepared by initially dissolving the Elvacite 2010 in the Exxate 700 and the cyclohexanone. The Kynar 301F was then dispersed in the resulting mixture using a high speed mixing blade from a Cowles mixer. The M-Pyrol was then added to the resulting mixture. Mixing was at room temperature so that the PVDF component remained as a dispersion in the mixture rather than dissolving. The dispersion clear coat was then coated on a casting sheet of polyester film by a reverse roll coater. The clear coat was then dried on the carrier sheet by the drying techniques described herein.

20 The solution clear coat was prepared by dissolving both resins in the solvent blend and by mixing with a high speed Cowles mixer to add sufficient heat to the mixture to completely dissolve the resin. The solution clear coat had substantially less solids (less than about 20% PVDF/ acrylic solids) than the dispersion clear coat along with use of stronger solvents to produce a clear solution PVDF/acrylic coating.

30 The dispersion color coat was prepared by dissolving the Elvacite 2042 in the DIBK and Cyclohexanone solvents along with the first part of the BLO solvent. The Kynar 301F was dispersed in the resulting mixture which was then diluted with the

35

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1 remaining BLO prior to adding the black dispersion. The
black dispersion comprised carbon black dispersed in
Elvacite 2042 and cyclohexanone.

5 The solution color coat was prepared by dissolving
both resins in the solvent and then adding the black
dispersion. The color coats were cast on separate
polyester casting sheets, rather than coating them over
a dried clear coat. If the base coat is cast over a
10 dried clear coat, the solvents in the base coat attack
the clear coat, especially in a solution-form base coat
with its stronger solvents. Both color coats were then
dried on their respective casting sheets.

Four thermoformable laminates were then prepared
for testing gloss and DOI. Various combinations of
15 dispersion clear coat, dispersion color coat, solution
clear coat, and solution color coat PVDF/acrylic
laminates, as described below, were prepared. Each
thermoformable laminate comprised a color coat and clear
coat laminated to an 18 mil ABS sheet. The color coat
20 was first laminated to the ABS backing sheet, the
polyester casting sheet was stripped away, then the
clear coat was laminated over the color coat and the
polyester casting sheet for the clear coat was then
stripped away, leaving an ABS thermoformable laminate
25 with the color coat and exterior clear coat bonded to a
face of the backing sheet. The backing sheet was then
subjected to deep draw thermoforming using a pressure
assist (thermoforming temperatures were approximately
270-280°F) to produce the test panels which were then
30 measured for gloss and DOI levels.

Comparative tests of gloss and DOI for the
dispersion and solution paint coats revealed the
following results:

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	<u>Laminate</u>	<u>20° gloss</u>	<u>60° gloss</u>	<u>DOI</u>
1	Dispersion clear coat/ Dispersion color coat	66	82	72
5	Solution clear coat/ Dispersion color coat	69	82	82
10	Dispersion clear coat/ Solution color coat	65	81	70
15	Solution clear coat/ Solution color coat	70	81	89

These test results demonstrated that higher levels of DOI are achieved by using the solution PVDF/acrylic coatings compared with similar dispersion coatings. Moreover, the DOI levels are high, greater than about 80 units and approaching 90 units in one instance, when the laminate includes at least a clear coat of solution-form PVDF/ acrylic resin. 60° gloss levels remained about the same for solution and dispersion coatings, and these gloss levels were sufficiently high to meet exterior automotive requirements. 20° gloss levels were somewhat higher with the solution clear coat films. Best results were obtained when the paint coat comprised both a clear coat and an underlying color coat of the solution PVDF/acrylic resin.

Example 12

The chemical resistance properties of the PVDF/acrylic paint coats of this invention were compared with three other commercially used automotive paint systems. The results demonstrated that the paint coat

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1 of this invention exhibited the best chemical
resistance. Two panels comprising PVDF/methyl
methacrylate clear coats according to this invention
were tested for chemical resistance (acid/alkali
5 spotting). Three additional test panels comprised clear
coats and pigmented base coats made from commercially
available thermoplastic lacquer automotive paint systems
which comprised dispersions of polymethyl methacrylate
copolymers. Two additional tests panels comprised a
10 rigid enamel, i.e., a melamine acrylic thermoset
exterior automotive paint, and a flexible enamel, i.e.,
a flexible melamine polyester thermoset exterior
automotive paint. Several test solutions were used,
including organic acids, G.M. acid rain, and various
15 concentrations of sulfuric acid, hydrochloric acid and
sodium hydroxide. The paint coats of this invention
achieved the highest rating and were untouched by the
different test solutions. Each of the commercial
automotive paints experienced etching by one or more of
20 the test solutions.

Thermoplastic Polyolefin Backing Sheet and Substrate

Thermoplastic polyolefins (TPO's) such as
polypropylene and polyethylene are useful as a car body
25 substrate material because of their impact resistance,
corrosion resistance, and their ability to be formed
into different complex configurations. Previously,
TPO's have been difficult to paint and this has limited
their use in the automotive market. Adhesion of the
30 paint coat to the TPO substrate, particularly, has been
a problem. The process of this invention can be used to
produce an automotive quality paint coat on a TPO car
body panel, and good adhesion can be produced between
the paint coat and the TPO composite structure forming
35 the underlying car body panel.

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1 Briefly, in this embodiment of the invention, a
thin size layer of a thermoplastic chlorinated
polyolefin (CPO) is coated between the paint coat layer
on the flexible carrier film and the flexible TPO
5 backing sheet. This composite structure is then
thermoformed and bonded to a thick rigid layer of a TPO
resin forming the substrate base for the composite car
body panel.

The size coat is preferably made from a coating
10 composition of a solution of the CPO. The coating
composition contains about 10-60% by weight of the CPO
and correspondingly about 40-90% by weight of solvent.
Any conventional solvent can be used that will dissolve
the CPO such as toluene or xylene. The CPO preferably
15 is a chlorinated polypropylene or chlorinated
polyethylene containing up to about 50% by weight
chlorine and preferably about 15-50% by weight chlorine.
One preferred chlorinated polypropylene is a
propylene/maleic anhydride copolymer chlorinated to a
20 level of about 15-50% by weight chlorine. One
particularly preferred chlorinated polypropylene
comprises polypropylene and maleic acid containing about
18-35% by weight chlorine and having an acid no. of
about 15.

25 The flexible backing sheet and the rigid substrate
layer of the composite car body panel are prepared from
standard automotive quality TPO resins, typically a
polypropylene resin.

The TPO composite of this invention provides
30 automotive manufacturers with many advantages over prior
art compositions. Adhesion problems with recessed
portions of a part are minimized, solvent emissions
associated with spray painting, the need for expensive
hangers and jigs to maintain shape of a plastic part
35 during baking, and the need for a primer which is

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1 required in a conventional paint spraying process all
are eliminated. Additionally, the composite has a
unique set of characteristics that make it superior to
conventional injection molded and spray painted parts.

5 The color coat/clear coat of the composite of this
invention can be cured at temperatures in excess of
200°C versus a maximum of 125°C for conventional
injection molded and spray painted plastic parts. This
allows for the use of paint chemistries which cannot be
10 used with conventional TPO parts. For example, the
fluorocarbon polymers of this invention can be used and
are substantially more durable and chemical resistant
than conventional low bake paints.

The TPO used for the flexible backing sheet can be
15 of a different quality than the TPO used for the rigid
substrate layer of the composite. Presently, in the
formation of injection molded automotive parts from TPO
resins, the TPO resin must be of the highest quality,
i.e., free of gel particles and any foreign matter, to
20 ensure that a defect free part is formed with an
automotive quality surface. Since the surface quality
of the composite of this invention is determined by the
surface of the flexible backing sheet, only the backing
sheet need be of a high quality TPO resin, while the
25 rigid substrate layer of the composite can be of a lower
quality TPO resin, for example, that may contain gel
particles and not affect the appearance of the resulting
part or the structural integrity of the part.

The ability to separate the surface characteristic
30 of the composite from the injection molded resin used to
form the rigid layer of the composite allows for the
formation of greatly improved auto parts. For example,
fiberglass reinforced or other filler reinforced TPO's
can be used for the injection molding resin for the
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1 rigid layer of the composite, and stronger and more rigid parts can be formed than has been possible before.

The following example illustrates use of the TPO composite structure in a car body panel.

5

Example 13

A thermoformed thermoplastic polyolefin (TPO) quarter panel for a Pontiac Fiero having an exterior high gloss jet black automotive paint was formed. The paint coat was first coated onto a surface of a sheet of flexible polyester film. The film is a 50 micron thick high gloss duPont Mylar 200A polyester film. The paint layers coated onto the film were a clear coat, a color coat and a chlorinated polyolefin size coat. Each was coated onto the polyester film in that order.

15

A clear coating composition was prepared as follows:

<u>Ingredient</u>	<u>Parts</u>
Methylethyl ketone	40.85
20 Butyrolactone	40.85
Elvacite 2021 - (Polymethyl methacrylate having a weight average Mw of 200,000)	6.22
UV absorber [Tinuvin 900-2-hydroxy-3,5-di[1,1-dimethyl(benzyl)phenyl]-2H-benzotriazole]	0.35
Hindered amine light stabilizer-[Tinuvin 292-bis(1,2,2,6,6-pentamethyl-4 piperidiny]sebacate]	0.18
30 Kynar 301F	11.15

The solid ingredients were added to the methyl ethyl ketone and butyrolactone solvents with mixing and mixing was continued until dissolved. The film forming binder of the coating contained about 65% PVDF and 35%

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1 polymethyl methacrylate. The clear coating was applied
by reverse roll coater to the polyester film. The clear
coat was dried on the polyester film by passing it
through a multi-zone impinging air drying oven having
5 three heating zones spaced apart axially along the
length of the carrier, with each drying zone having a
progressively higher temperature. The clear-coated
polyester sheet was passed through the heating zones at
a line speed of about 7.5 meters per minute; each
10 heating zone was about 12 meters long. Temperatures of
the three heating zones were: Zone 1: 125°C; Zone 2:
165°C; Zone 4: 200°C. By passing the clear coated
polyester sheet through the three heating zones,
substantially all solvent gases from the clear coat were
15 removed to produce a dry clear coat of uniform film
thickness about 20 microns thick.

A jet black color coating composition was
formulated as follows:

	<u>Ingredient</u>	<u>Parts</u>
20	Cyclohexanone	9.27
	Diisobutyl ketone	18.54
	Butyrolactone	8.34
	Elvacite 2042 =(polyethyl methacrylate having a weight average Mw 300,000)	10.02
25	Solsperse 17,000 Dispersing agent	0.10
	Kynar 301F	24.04
	Butyrolactone	14.14
	Black Pigment Dispersion	15.00

30 The black pigment dispersion comprised carbon black
in a vehicle of Elvacite 2043 (polyethyl methacrylate)
available commercially as Gibraltar 438-39110 pigment.

The color coating composition was prepared by first
dissolving the acrylic resin in the cyclohexanone,
35 disobutyl ketone and butyrolactone solvents at a

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1 temperature of about 55°C and then allowing it to cool
before the polyvinyl fluoride component was added to the
mixture to form a dispersion of the PVDF in the acrylic
resin. The black pigment dispersion was then added to
5 the resulting mixture to produce the jet black color
coating composition. On a weight basis, the amount of
pigment contained in the color coating was about 4-5%.
The binder of the coating contained about 65% PVDF and
35% acrylic resin by weight. The acrylic resin
10 component comprised about 90% Elvacite 2042 and 10%
Elvacite 2043. The color coating composition was coated
onto the dried clear coat as above and then passed
through the three stage oven described above to dry the
color coating and form a dry color coating layer about
15 20 microns thick.

A CPO (chlorinated polyolefin) size coating
composition for use with a TPO backing sheet was
formulated as follows:

	<u>Ingredient</u>	<u>Parts</u>
20	Xylene	24.60
	Chlorinated polyolefin (CPO) solution (Eastman's CP-343-1 25% solids in xylene of chlorinated polypropylene/maleic acid polymer, acid no. about 15, chlorine 25 content about 18-23%)	25.00
	Toluene	42.50
	N-methyl pyrrolidone	1.00
	Acrylic Dispersion Resin (60% solids of an acrylic 30 vinyl oxazoline ester polymer described in Example 1 of Miller U.S. Patent 3,844,993)	6.90

The binder of the size coating composition
35 contained about 60% CPO and about 40% acrylic resin by

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1 weight. The size coat composition was coated onto the
dried color coat to a dry film thickness of about 2.5
microns using the reverse roll coater. The three
5 temperature zones were maintained at the same
temperature as used for the clear and color coats but a
carrier speed 30 meters per minute was used.

The resulting paint coated polyester film was then
passed to a laminating operation illustrated in FIG. 2,
where the paint coat of the polyester film was
10 transferred to a 500 micron thick TPO backing sheet made
from RPI E-1000, thermoplastic olefinic elastomer from
Republic Plastics Company, to form a face sheet. RPI E-
1000 has a flexural modulus of approximately 690 MPa and
a melt flow rate of approximately 0,8 g/10 min. In the
15 laminating operation, the backing sheet and the paint
coated polyester film carrier were run at a lineal speed
of 5 meters per minute, and the laminating drum was
operated at a temperature of 177°C. The CPO size coat
was heat activated and the paint coat was transferred
20 from the polyester film to the face of the TPO backing
sheet during the laminating operation, in which the hot
steel drum applied a force of about 54 kg/lineal cm to
form the face sheet. The polyester film was stripped
away from the surface of the face sheet, leaving the
25 paint coat bonded to the TPO sheet, with the clear coat
providing a high gloss surface on the exterior of the
TPO backing sheet.

The resulting face sheet was then thermoformed into
a complex three-dimension shape to form a plastic
30 quarter panel molding. In the thermoforming process,
the face sheet was first heated to a temperature of
about 121°C to soften the face sheet. The heated face
sheet then was placed over a pressure assist vacuum
former buck and a vacuum was drawn against the buck on
35 the TPO side of the face sheet and 2.1 kg/cm² gauge of

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1 air pressure applied on the clear coat side of the
laminate to form the heated face sheet into the three
dimensional shape of the quarter panel.

5 The resulting thermoformed laminate was then
trimmed to fit in the mold cavity of a plastic injection
molding machine. A quarter panel was then formed. An
elastomeric thermoplastic alloy molding resin RTA-3263
from Republic Plastics Company, having a flexural
modulus of about 1725 MPa was used for forming the base
10 of the quarter panel. The resin was injected into the
mold behind the thermoformed laminate, fusing the resin
to the TPO base of the laminate to form the quarter
panel about 2.5-3.75 mm thick. The mold was operated at
the normal melt temperature for the resin. A quarter
15 panel was formed that is in an integral plastic
composite part with a defect-free paint coat on the
exterior surface of the panel.

The quarter panel was tested and the tests
demonstrated the usefulness of the paint coat as an
20 exterior automotive finish. The test results indicated
that desirable appearance properties, including gloss,
were produced. Specular reflectance measured units 70
units at 20° gloss and DOI measured 85 units. Color
uniformity was good. The test results also demonstrated
25 a desirable combination of durability properties. The
test panel passed tests for gasoline resistance, acid
resistance, chip resistance (gravelometer reading of 9),
impact resistance (80 in./lb. for Gardner Test), and
passed QUV and 96 hour humidity exposure tests.

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Water Soluble Protective Coatings

As disclosed previously, a thin film of wax can be
coated onto the flexible carrier sheet prior to casting
the clear coat onto the carrier. The wax film can serve

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1 as a protective layer for the finished painted car body panel.

5 In addition, a separate water soluble protective coating can be applied to the clear coat (or to the wax film on the clear coat) during processing so that the water soluble layer is available to provide a protective mar resistant exterior coating for the finished car body panel, through assembly of the automobile and shipment to the purchaser. The coating is preferably a low
10 molecular weight material which adheres to the clear coat throughout processing and can be buffed to a glossy finish.

15 Preferably, the water soluble protective coating is over stamped as a barrier film onto the dried clear coat. The clear coat and color coat are cast on a polyester carrier film and bonded to the flexible backing sheet as described previously. Separately, a water soluble coating such as polyvinyl alcohol (PVA) is coated onto a flexible polyester carrier sheet and dried. After the
20 carrier film is stripped away from the surface of the clear coat, the PVA film is over stamped onto the surface of the clear coat, preferably by pressure roll techniques. The PVA is separately cast so that it is not subjected to solvent attack from the clear coat and so that it would not interfere with the transfer of
25 gloss to the surface of the clear coat from the polyester casting film. The polyester carrier film is then stripped away from the PVA layer, leaving a water soluble protective film of PVA bonded to the exterior surface of the clear coat. The resulting backing sheet
30 is then subjected to further processing, including thermoforming and injection-cladding, leaving a finished car body panel with the water soluble protective outer coating. This coating can then be easily buffed or
35 removed with water by the auto dealer or purchaser.

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1

Controlled Flop/Head-on Brightness

The color coats used in this process can include metallic flake pigments. When a metallic flake pigment
5 dries on a substrate surface, the flakes generally become oriented in parallel to the surface of the substrate. These orientations can vary, however, especially with spray painting, which can cause substantial disorientation and resulting differences in
10 the apparent color of the finished paint. Visual color comparisons of metallic paints can be made by known procedures for measuring such parameters as flop index and head-on brightness (HOB). (These measurements are described in U.S. Patent No. 4,692,481 to Kelly, which
15 is incorporated herein by this reference.) A finished paint coat with well-oriented metallic flakes has desirable high flop and HOB values. The process of this invention can be used to produce a finished metallic flake paint coat with high flop and HOB values. The
20 metallic flake color coat can be coated separately onto its polyester carrier film and slowly dried on the film to carefully align the metallic flakes in a parallel orientation, achieving high flop and HOB values. The pre-aligned metallic flake pigment is then subjected to
25 further processing (transfer to the backing sheet, thermoforming, and injection-cladding, for example) to produce a finished car body panel with the high flop and HOB values. The linear orientation of the flakes is not disrupted during further processing and is thought to be
30 enhanced by the elongation occurring during thermoforming. The high values for flop and HOB are substantially higher than with spray painting a similar substrate.

In addition, even higher HOB values are produced
35 when the paint coat of this invention uses metallic

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1 flakes with a thickness of less than about 2000
Angstroms. An example of these flakes is available from
Avery Decorative Film Division of Avery International.
These metallic flakes are sold as L-53520 and identified
5 as Bright Aluminum Flake. The paint coat of this
invention, when using these metallic flakes, can achieve
an HOB value of greater than 140 units, for a pure
silver color coat.

10 Pigmented Backing Sheet

Improvements can be provided by using a pigmented
backing sheet in the process of this invention.
Experiments have shown that light transmission through a
paint-coated laminate is reduced when a pigmented
15 backing sheet is used in the process, as compared with a
clear backing sheet. These experiments included
measuring light transmission through a white paint coat
laminated to a black backing sheet (the paint coat
comprised a clear coat and underlying white color coat),
20 compared with measuring light transmission through the
same white paint coat laminated to a clear backing
sheet. The pigmented backing sheet increases opacity
substantially, thereby reducing the amount of pigment
required in the color coat to hide defects in the
25 underlying substrate.

Pre-Applied Graphics

Printed graphics can be incorporated into the
process of this invention. In one process for applying
30 graphics to the finished paint coat, the clear coat is
first cast onto the flexible polyester carrier film.
The clear coat is then dried on its carrier film. The
graphics pattern is then printed on the surface of the
dried clear coat opposite from the carrier film. The
35 graphics pattern can be any desired pinstriping pattern,

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1 for example. The color coat also is cast on the clear
coat and over the graphics pattern and dried. This
leaves the clear coat on its carrier film with the pre-
applied graphics and color coat visible through the
5 clear coat. Alternatively, the color coat can be cast
in a separate carrier film and then transferred in dry
film form over the pre-printed graphics pattern and onto
the dried clear coat. A suitable size coat is then
applied to the surface of the dried color coat, and the
10 resulting laminate is transferred to the flexible
backing sheet by the techniques described previously.
The carrier film is stripped away in this process, and
the resulting paint-coated laminate is thermoformed into
the desired shape to form a mold insert. The resulting
15 mold insert is then injection clad with the desired
substrate material to form the finished car body panel.
An advantage of this process is that graphics patterns
are printed under an automotive quality clear coat,
which provides a smooth exterior surface on the finished
20 car body panel protecting the underlying graphics. The
graphics are therefore not subject to wax or dirt build-
up around them as is the case presently with graphics
applied to the surface of a finished exterior paint
coat.

25

Thus, the present invention provides a dry paint
process and paint system which produce a useful blend of
durability, chemical and visual appearance properties.
The paint coat has a combination of durability, gloss,
30 resistance to deglossing, and elongation that produce
and retain exterior automotive properties in the paint
coat throughout the processing steps. As one advantage,
the invention makes it possible to use high molecular
weight PVDF in an OEM exterior paint for plastic car
35 bodies, despite the temperature limitations of molded

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1 plastic materials and the fact that PVDF normally
requires use of strong solvents and high temperatures to
form glossy films from this polymer. By alloying PVDF
polymers with acrylic polymers, the result is a paint
5 coat with superior mechanical properties, including
exterior durability, chemical resistance and toughness.
The low surface energy surfaces characteristic of
fluoropolymers also provide enhanced washability and
produce a high contact angle "beading" surface requiring
10 little or no waxing. As a further advantage, the dry
paint process allows part production and coating to be
coincidental with the other manufacturing operations at
an automobile production plant by transferring quality
control, solvent emission problems and color control to
15 an outside supplier. This can eliminate from the auto
plant the conventional coating operations, including
application lines and ovens.

As a further advantage, the dry paint process can
be extended to producing a flexible self-adhesive
20 laminate for use in automotive refinishing. Fig. 14
illustrates one embodiment of such a laminate 140 which
can allow rapid refinishing of an exterior automotive
paint coat with greatly reduced surface preparation
requirements. The flexible laminate comprises a
25 removable masking 141, the clear coat 45 bonded to the
color coat 46 (although a single paint coat having
exterior automotive properties can be used as an
alternative to the separate clear coat and color coat),
a flexible backing 142 adhered to the color coat 46, a
30 pressure-sensitive adhesive 144 on the flexible backing,
and a release backing 146 covering the pressure-
sensitive adhesive. This laminate can be tolerant to
rough surfaces and develop good adhesion because of the
conformability provided by its flexibility and the
35 pressure-sensitive adhesive backing. By applying a

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1 trimmable self-adhesive sheet for large and small areas,
it can have application to skilled refinishers as well
as use for the consumer market by eliminating the need
for large paint booths and ovens, capital investment,
5 and environmental emission problems normally associated
with exterior automotive refinishing.

Although the invention has been described as
relating to automotive quality paint coats applied to
car body panels, it is to be understood that the
10 invention is not limited solely to automotive uses or
exterior automotive panels. The invention is also
applicable to other vehicles requiring automotive-
quality exterior paint coats. Trucks, motorcycles,
boats, dune buggies, and the like are examples.
15 Moreover, the invention is applicable to a variety of
exterior body members or parts of motor vehicles.
Bumpers, fender extensions, wheel covers, hub caps, trim
rings for wheels, lamp housings, grills and other
exterior facia components or parts are examples of other
20 substrates to which the paint coat can be applied, in
addition to conventional exterior body parts or panels
of the vehicle.

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1 WHAT IS CLAIMED IS:

1. A process for applying a paint coat, suitable for exterior automotive use, to a plastic exterior body panel of a motor vehicle, characterized by the steps of:
- 5 applying a clear coat (45) of a synthetic resinous material in thin film form onto a surface of a flexible casting sheet (42), and drying the clear coat on the casting sheet, the surface of the sheet having a specular reflectance for transferring to the surface of
- 10 the dried clear coat a gloss level sufficient for exterior automotive use;
- forming a color coat (46) of a pigmented synthetic resinous material which is dried and adhered to the clear coat;
- 15 transferring the dried clear coat and color coat to a semirigid backing sheet (72) of a synthetic resinous material to form a composite paint coat (44) bonded to a face of the backing sheet, in which the clear coat forms the exterior surface of the transferred
- 20 paint coat and the color coat is bonded between the clear coat and the face of the backing sheet, and in which the exterior surface of the clear coat substantially retains the gloss transferred to it from its casting sheet;
- 25 thermoforming the backing sheet and the composite paint coat thereon to form a three-dimensionally shaped preformed laminate (116); and
- placing the preformed laminate in a mold and molding a synthetic resinous substrate material (118) to
- 30 the preformed laminate to form an exterior vehicle body panel (130) with a finished exterior automotive paint coat;
- the clear coat comprising a material that substantially retains said gloss level during the
- 35 thermoforming step; the backing sheet having sufficient

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1 thickness and sufficient elongation to absorb defects
present in the substrate material to retain an
essentially defect-free gloss on the clear coat surface
following adherence of the laminate to the substrate
5 material; the finished composite paint coat providing
sufficient appearance and durability properties for use
as an exterior automotive paint coat.

2. The process according to claim 1,
10 characterized in that the laminate (116) is thermoformed
at a temperature greater than about 270°F, and the
composite paint coat (44) elongates greater than about
40% during the thermoforming step while still retaining
said gloss level and said exterior automotive appearance
15 and durability properties.

3. The process according to claim 1,
characterized in that the clear coat (45) comprises a
fluorinated polymer and acrylic resin-containing
20 material.

4. The process according to claim 3,
characterized in that the clear coat (45) comprises a
thermoplastic paint system in which the fluorinated
25 polymer is selected from the group consisting of
polyvinylidene fluoride, and copolymers and terpolymers
of vinylidene fluoride.

5. The process according to claim 4,
30 characterized in that the dried clear coat (45) contains
less than about 70% polyvinylidene fluoride and less
than about 50% acrylic resin, by weight of the total
acrylic resin and PVDF solids present in the clear coat.

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1 6. The process according to claim 1,
characterized in that the paint coat (44) has the
minimum levels of gloss, distinctiveness-of-image, QUV,
gasoline resistance, cleanability, acid resistance,
5 hardness, abrasion resistance and impact strength,
substantially as defined in the automotive
specifications for exterior automotive paint finishes
described herein.

10 7. The process according to claim 1,
characterized in that the preformed laminate (116) is
molded to the substrate material (118) by injection
cladding, reaction injection molding, or thermoset sheet
molding techniques.

15 8. The process according to claim 1,
characterized in that the clear coat (45) applied to the
casting sheet (42) comprises a thermoplastic paint
system which includes polyvinylidene fluoride and an
20 acrylic resin, in which the polyvinylidene fluoride is
dispersed in a solution of the acrylic resin.

25 9. The process according to claim 1,
characterized in that the clear coat (45) applied to the
casting sheet (42) comprises a thermoplastic paint
system comprising a solution of polyvinylidene fluoride
and acrylic resin.

30 10. The process according to claim 9,
characterized in that the finished paint coat (44) has a
60° gloss level greater than about 75 gloss units and a
distinctiveness-of-image level greater than about 80
units.

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1 11. The process according to claim 1,
characterized in that the backing sheet (72) is a
semirigid sheet with a thickness in the range from about
10 mils to about 40 mils.

5

 12. The process according to claim 1,
characterized in that the backing sheet (72) is made
from a material selected from the group consisting of
ABS, polyester, amorphous nylon, and thermoplastic
10 polyolefins, including polypropylene and polyethylene.

 13. The process according to claim 1,
characterized by including applying a thin film of wax
to the casting sheet (42) prior to casting the clear
15 coat (45) on the casting sheet.

 14. The process according to claim 1,
characterized in that a graphics pattern is printed
between the clear coat (45) and the color coat (46).

20

 15. The process according to claim 1,
characterized by a pigment contained in the backing
sheet (72).

25 16. The process according to claim 1,
characterized by metallic flakes contained in the color
coat (46), in which the flakes are aligned linearly when
coated on a carrier film.

30 17. The process according to claim 1,
characterized in that a water soluble protective coating
on the exterior surface of the paint coat (44).

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1 18. The process according to claim 17,
characterized by the protective coating is over stamped
on the clear coat (45).

5 19. The process according to claim 1,
characterized in that the thermoforming step is carried
out by avoiding contact between the thermoforming
apparatus (112) and the clear coat (45) side of the
backing sheet (72).

10 20. A thermoformable laminate for use in forming
an exterior portion of an exterior car body panel, the
laminate comprising a thin, semirigid backing sheet made
from a synthetic resinous material, and an automotive
15 quality paint coat bonded to a face of the backing
sheet, in which the paint coat includes a synthetic
resinous coating in dry thin film form having an
exterior surface with a predetermined gloss level
transferred to it from a high gloss casting sheet, the
20 paint coat having sufficient elongation and resistance
to deglossing such that the laminate is thermoformable
into a highly contoured three-dimensional shape while
the paint coat substantially retains said predetermined
gloss level during thermoforming and provides
25 predetermined appearance and durability properties
sufficient to be useful as an exterior automotive paint
coat following thermoforming of the laminate.

30 21. The article according to claim 20 in which the
laminate can be thermoformed at a temperature of at
least about 270°F, and the paint coat elongates greater
than about 40% during thermoforming at said
thermoforming temperature while still retaining said
gloss level and said appearance and durability
35 properties.

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22. The article according to claim 20 in which the paint coat comprises a fluorinated polymer and acrylic resin-containing paint system with thermoplastic properties, in which the paint coat has been coated on a casting sheet and dried and then transferred from the casting sheet to the backing sheet.

5

23. The article according to claim 20 in which the paint coat comprises a thermoplastic paint system which includes polyvinylidene fluoride and an acrylic resin.

10

24. The article according to claim 23 in which the dried paint coat contains less than about 70% polyvinylidene fluoride and less than about 50% acrylic resin, by weight of the total PVDF and acrylic resin components contained in the paint coat.

15

25. The article according to claim 20 in which the paint coat comprises a pigmented synthetic resinous material with thermoplastic properties.

20

26. The article according to claim 20 in which the paint coat comprises an exterior clear coat and an underlying color coat bonded to the clear coat.

25

27. The article according to claim 26 in which the color coat contains a highly dispersed pigment, and in which the clear coat comprises a thermoplastic coating principally containing a fluorinated polymer and an acrylic resin.

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1 28. The article according to claim 27 in which the
clear coat is a thermoplastic paint system which
consists essentially of about 50% to about 70%
polyvinylidene fluoride and about 30% to about 50%
5 acrylic resin; and in which the acrylic resin component
comprises polymethyl methacrylate, polyethyl
methacrylate, or mixtures thereof, including copolymers
thereof.

10 29. The article according to claim 28 in which the
color coat also consists essentially of about 50% to
about 70% polyvinylidene fluoride and about 30% to about
50% acrylic resin; and in which the acrylic resin
component comprises polymethyl methacrylate, polyethyl
15 methacrylate, or mixtures thereof, including copolymers
thereof.

 30. The article according to claim 20 in which the
paint coat on the thermoformed laminate has at least the
20 minimum levels of gloss, distinctiveness-of-image, QUV,
hardness, impact resistance, cleanability, acid
resistance, gasoline resistance, and abrasion
resistance, substantially as defined in the automotive
specifications for exterior automotive paint finishes
25 described herein.

 31. The article according to claim 20 in which the
paint coat includes a fluorinated polymer selected from
the group consisting of polyvinylidene fluoride, and
30 copolymers and terpolymers of vinylidene fluoride.

 32. The article according to claim 20 in which the
paint coat has a 60° gloss level greater than about 75
gloss units and a distinctiveness-of-image level greater
35 than about 80 units.

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33. The article according to claim 20 in which the backing sheet is a semirigid sheet with a thickness in the range from about 10 mils to about 40 mils.

5

34. The article according to claim 20 in which the backing sheet is made from a material selected from the group consisting of ABS, polyester, amorphous nylon, thermoplastic polyolefins, including polypropylene and polyethylene.

10

35. The article according to claim 20 including a wax film applied to the outer face of the clear coat from the casting sheet.

15

36. The article according to claim 20 in which a graphics pattern is printed between the paint coat and backing sheet and is visible through the paint coat.

20

37. The article according to claim 20 including a pigment contained in the backing sheet.

38. The article according to claim 20 including a metallic flake paint layer contained in the paint coat.

25

39. The article according to claim 20 including a water soluble protective coating on the exterior surface of the paint coat.

30

40. An exterior plastic body panel for motor vehicles, the panel having a synthetic resinous automotive quality paint coat bonded to a synthetic resinous thermoformable backing sheet to form a laminate in which the exterior surface of the paint coat has exterior automotive gloss and distinctiveness-of-image

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1 levels, and in which the laminate has been thermoformed
into a three-dimensional shape and adhered to a plastic
substrate to form said plastic exterior body panel, the
paint coat having sufficient elongation and resistance
5 to deglossing to have substantially maintained said
gloss and distinctiveness-of-image levels during
thermoforming, the backing sheet having sufficient
thickness and elongation to have absorbed defects in the
substrate material, thereby providing said paint coat on
10 the finished body panel with an essentially defect-free
surface with the appearance and durability properties
sufficient for exterior automotive use.

41. The panel according to claim 40 in which the
15 paint coat comprises a thermoplastic fluorinated polymer
and acrylic resin-containing paint system.

42. The panel according to claim 40 in which the
finished paint coat has the minimum levels of gloss,
20 distinctiveness-of-image, QUV, gasoline resistance,
cleanability, acid resistance, hardness, abrasion
resistance, and impact strength, substantially as
defined in the automotive specifications for exterior
automotive paint finishes described herein.

25 43. The panel according to claim 40 in which the
paint coat comprises an exterior clear coat and an
underlying color coat bonded to the clear coat.

30 44. The panel according to claim 43 in which the
clear coat comprises a fluorinated polymer and acrylic
resin-containing material with thermoplastic properties.

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1 45. The panel according to claim 40 in which the
paint coat includes a fluorinated polymer selected from
the group consisting of polyvinylidene fluoride, and
5 copolymers and terpolymers of vinylidene fluoride.

5 46. The panel according to claim 40 in which the
paint coat has an 80° gloss level greater than about 75
gloss units and a distinctiveness-of-image level greater
than about 80 units.

10 47. The panel according to claim 40 in which the
backing sheet is a semirigid sheet with a thickness in
the range from about 10 mils to about 40 mils.

15 48. The panel according to claim 40 in which the
backing sheet is made from a material selected from the
group consisting of ABS, polyester, amorphous nylon, and
thermoplastic polyolefins including polypropylene and
polyethylene.

20 49. The panel according to claim 40 including a
wax film applied to the outer face of the clear coat
from the casting sheet.

25 50. The panel according to claim 40 in which the
preformed laminate is molded to the substrate material
by injection cladding, reaction injection molding, or
thermoset sheet molding techniques.

30 51. The panel according to claim 40 in which a
graphics pattern is printed between the paint coat and
backing sheet to be visible through the paint coat.

35 52. The panel according to claim 40 including a
pigment contained in the backing sheet.

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53. The panel according to claim 40 including metallic flakes contained in the paint coat.

5

54. The panel according to claim 40 including a water soluble protective coating on the paint coat.

10

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55. An exterior motor vehicle body panel comprising a plastic substrate, and a laminate on the exterior of the substrate, and a three-dimensionally thermoformed paint coat comprising a thermoplastic fluorinated polymer and acrylic resin-containing paint system that provides an exterior surface on said panel sufficient for exterior automotive use following thermoforming of said paint coat, and in which the amounts of the fluorinated polymer and acrylic resin contained in the paint system are sufficient to resist deglossing of the paint coat during the thermoforming step so that a gloss level is provided in the finished panel, together with sufficient appearance and durability properties for exterior automotive use.

25

56. The panel according to claim 55 in which the fluorinated polymer is selected from the group consisting of polyvinylidene fluoride, and copolymers and terpolymers of vinylidene fluoride.

30

57. The panel according to claim 55 in which the finished paint coat has a 60° gloss level greater than about 75 gloss units and a distinctiveness-of-image greater than about 80 units.

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1 58. The panel according to claim 55 in which the
paint coat has the minimum levels of gloss,
distinctiveness of image, QUV, hardness, impact
resistance, cleanability, acid resistance, gasoline
5 resistance, and abrasion resistance, substantially as
defined in the automotive specifications for exterior
automotive paint finishes described herein.

10 59. The panel according to claim 55 in which the
backing sheet is a semirigid sheet with a thickness in
the range from about 10 mils to about 40 mils.

15 60. The panel according to claim 55 in which the
backing sheet is made from a material selected from the
group consisting of ABS, polyester, amorphous nylon, and
thermoplastic polyolefins, including polypropylene and
polyethylene.

20 61. The panel according to claim 55 in which the
step of adhering the preformed laminate to the substrate
material comprises injection cladding, reaction
injection molding, or sheet molding compound techniques.

25 62. A method of manufacturing a plastic exterior
body panel for a motor vehicle having a paint coat with
exterior automotive appearance and durability
properties, the method comprising:

30 forming a laminate comprising a semirigid
synthetic resinous backing sheet having a synthetic
resinous paint coat adhered to a face of the backing
sheet by dry transfer from a casting sheet, in which an
exterior automotive gloss level is transferred to the
exterior surface of the paint coat from the casting
sheet;

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1 thermoforming the laminate into a three-dimensional shape; and

placing the formed laminate in a mold and molding a plastic substrate material to the formed
5 laminate to bond the laminate to the substrate and form a plastic car body panel with a finished paint coat;
in which the material comprising the paint coat substantially retains said gloss level during the thermoforming step; and

10 in which the backing sheet has sufficient thickness and elongation to absorb defects from the substrate material so that the finished paint coat retains said gloss level during the step of molding the laminate to the substrate panel,

15 the finished paint coat providing the appearance and durability properties sufficient for exterior automotive use.

63. The method according to claim 62 in which the
20 paint coat comprises a fluorinated polymer and acrylic resin-containing material.

64. The method according to claim 62 in which the
25 paint coat is cast as a thermoplastic paint system comprising a solution of polyvinylidene fluoride and acrylic resin.

65. The method according to claim 64 in which the
30 paint coat has a gloss level greater than about 75 gloss units and a distinctiveness-of-image level greater than about 80 units.

35

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1 66. The method according to claim 62 in which the
paint coat is cast as a thermoplastic paint system which
includes polyvinylidene fluoride and an acrylic resin,
and in which the polyvinylidene fluoride is dispersed in
5 a solution of the acrylic resin.

67. The method according to claim 62 in which the
laminate is adhered to the substrate by injection
cladding, reaction injection molding, or thermoset sheet
10 molding techniques.

68. The method according to claim 62 in which the
backing sheet is a semirigid sheet with a thickness in
the range from about 10 mils to about 40 mils.

15 69. The process according to claim 62 in which the
thermoforming step is carried out by avoiding contact
between the thermoforming apparatus and the paint coat
on the backing sheet.

20 70. A process for applying a paint coat, suitable
for exterior automotive use, to a plastic exterior body
panel of a motor vehicle, the process comprising the
steps of:

25 applying a clear coat of a solution of
vinylidene fluoride and acrylic resin in thin film form
onto a surface of a flexible casting sheet, and drying
the clear coat on the casting sheet, the surface of the
sheet having a specular reflectance for transferring to
30 the surface of the dried clear coat a gloss level
sufficient for exterior automotive use;

 casting a color coat of a pigmented solution
of vinylidene fluoride and acrylic resin in thin-film
form and drying the color coat;

35

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1 transferring the dried clear coat and color
coat to a semirigid backing sheet of a synthetic
resinous material to form a composite paint coat bonded
to a face of the backing sheet, in which the clear coat
5 forms the exterior surface of the transferred paint coat
and the color coat is bonded between the clear coat and
the face of the backing sheet, and in which the exterior
surface of the clear coat substantially retains the
gloss transferred to it from the casting sheet;

10 thermoforming the backing sheet and the
composite paint coat thereon to form a three-
dimensionally shaped preformed laminate; and

 adhering the preformed laminate to a synthetic
resinous substrate material to form an exterior vehicle
15 body panel;

 the clear coat substantially retaining said
gloss level during the thermoforming step; the backing
sheet having sufficient thickness and sufficient
elongation to absorb defects present in the substrate
20 material to retain an essentially defect-free gloss on
the clear coat surface following adherence of the
laminate to the substrate material; the composite paint
coat providing sufficient appearance and durability
properties for use as an exterior automotive paint coat.

25 71. The process according to claim 70 in which the
paint coat on the thermoformed laminate has a gloss
level greater than about 75 gloss units and a
distinctiveness-of-image level greater than about 80
30 units.

 72. The process according to claim 70 in which the
substrate is adhered to the laminate by injection
cladding, reaction injection molding, or sheet molding
35 compound techniques.

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73. The process according to claim 70 in which the backing sheet is a semirigid sheet with a thickness in the range from about 10 mils to about 40 mils.

5

74. The process according to claim 70 in which the backing sheet is made from a material selected from the group consisting of ABS, polyester, amorphous nylon, thermoplastic polyolefins, including polypropylene and polyethylene.

10

75. The process according to claim 70 in which the paint coat is cast as a solution of polyvinylidene fluoride and acrylic resin.

15

76. The process according to claim 70 in which the finished paint coat has the minimum levels of gloss, distinctiveness-of-image, QUV, gasoline resistance, cleanability, acid resistance, hardness, abrasion resistance, and impact strength, substantially as defined in the automotive specifications for exterior automotive paint finishes described herein.

20

77. The process according to claim 70 in which the color coat includes metallic flakes aligned linearly, and the flakes have an average thickness of less than about 2000 Angstroms.

25

78. The process according to claim 77 in which the metallic flakes have a head-on brightness value greater than about 140 units.

30

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1 79. The process according to claim 1 in which the
color coat includes metallic flakes aligned linearly,
and the flakes have an average thickness of less than
about 2000 Angstroms.

5

80. The process according to claim 79 in which the
metallic flakes have a head-on brightness value greater
than about 140 units.

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Fig. 1

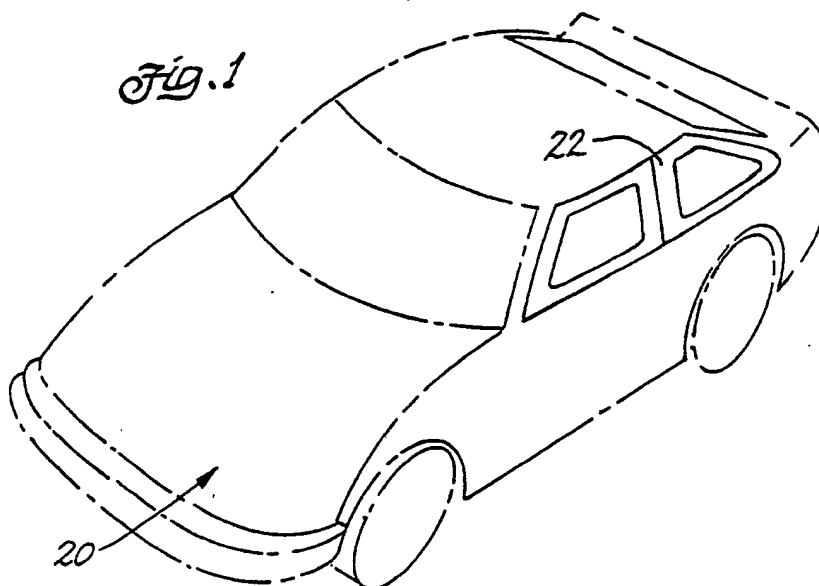


Fig. 2

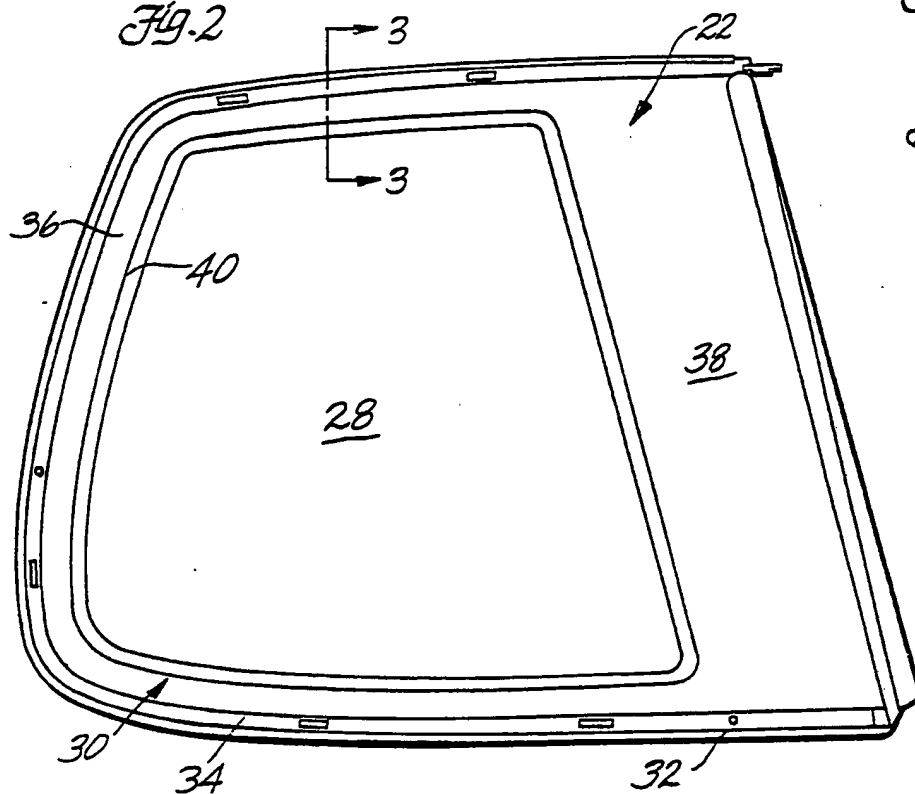


Fig. 3

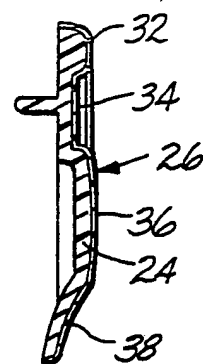
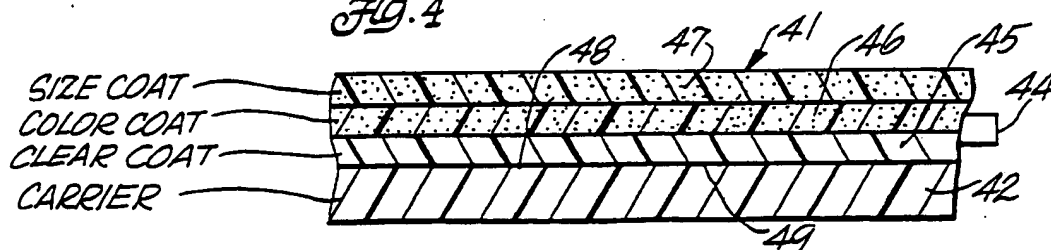


Fig. 4



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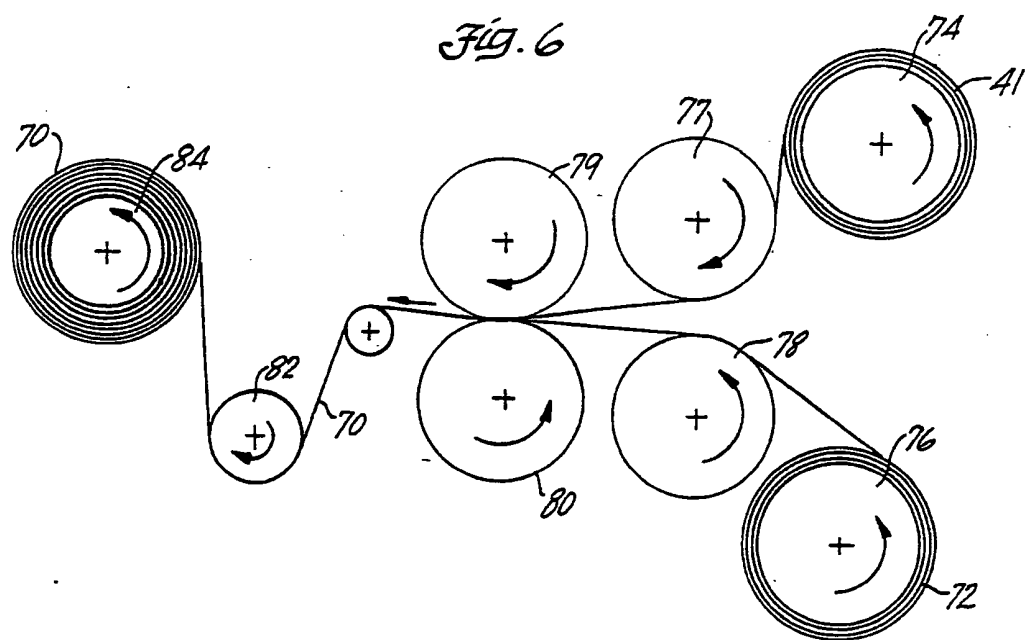
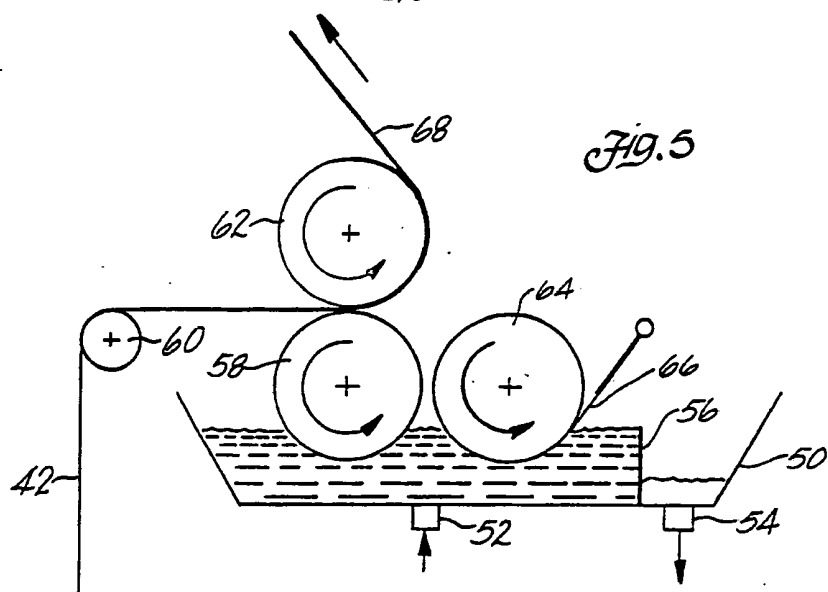


Fig. 7

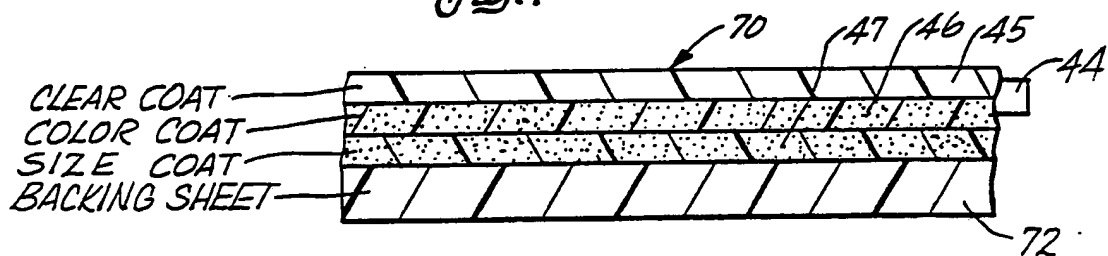


Fig. 8

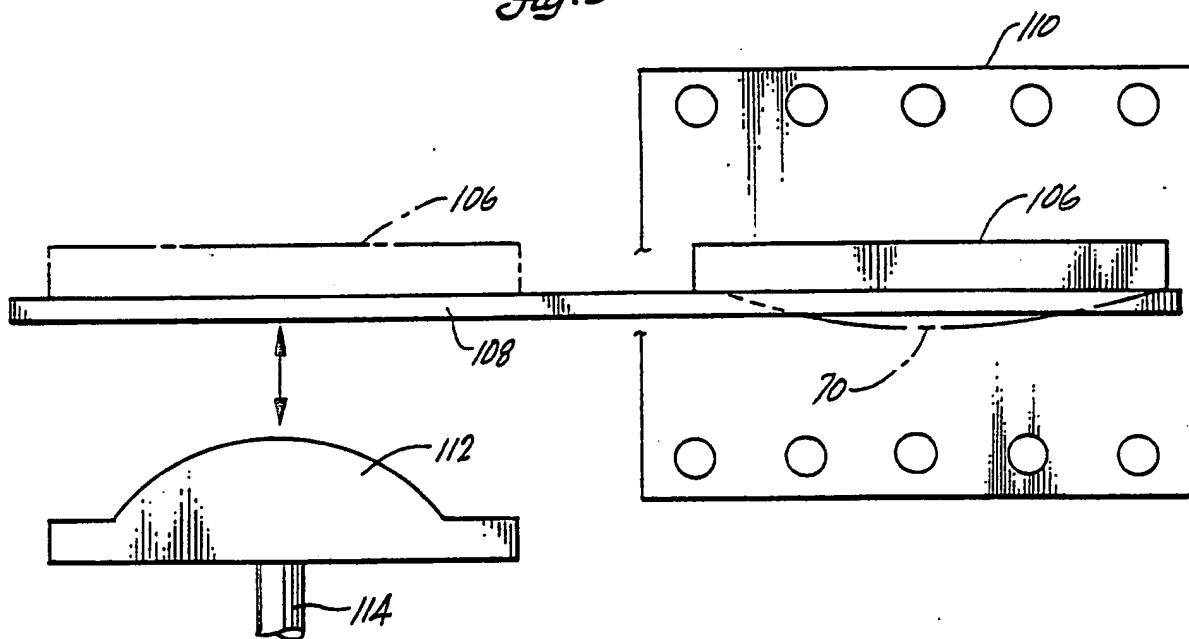


Fig. 9

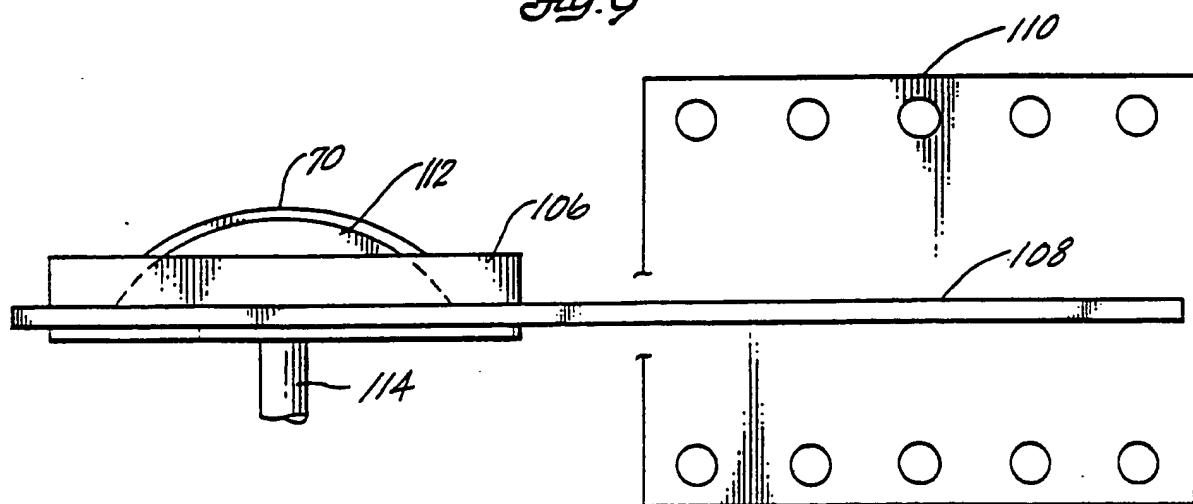


Fig. 10

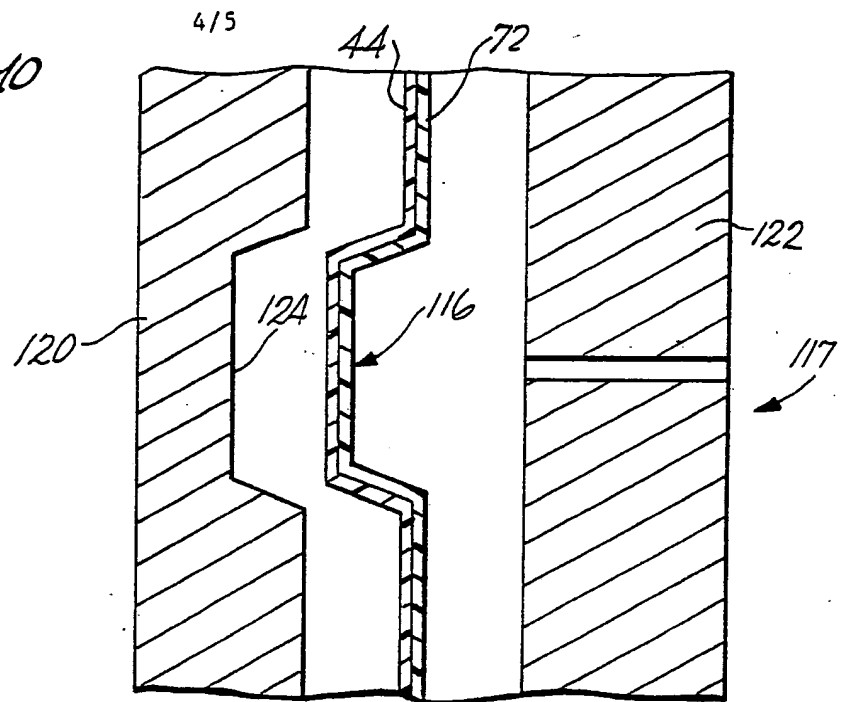


Fig. 11

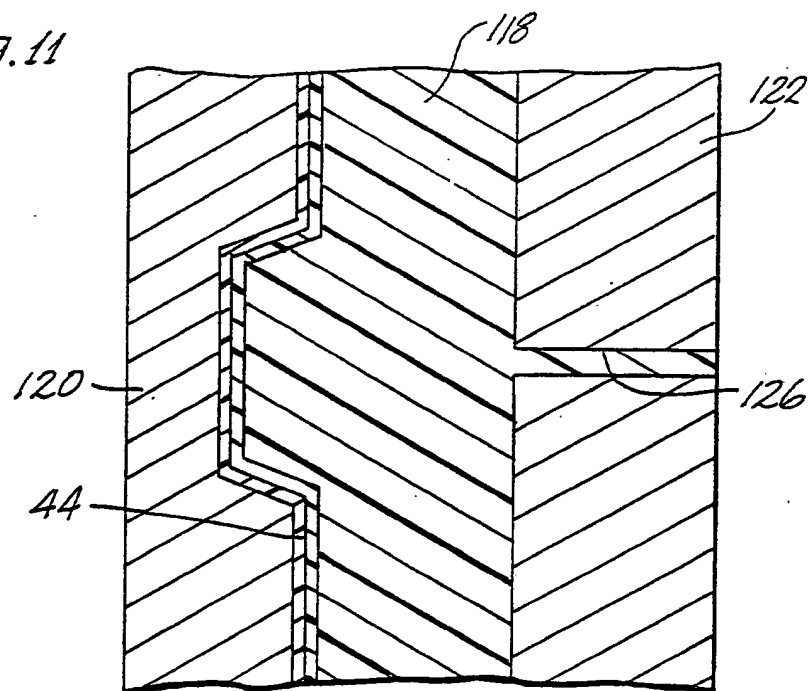
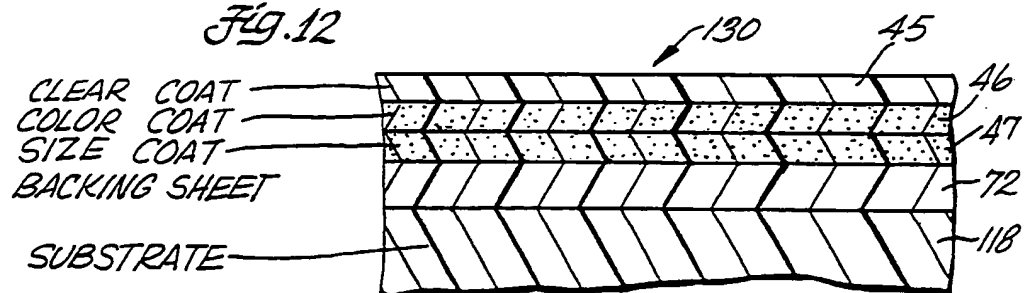


Fig. 12



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Fig. 13

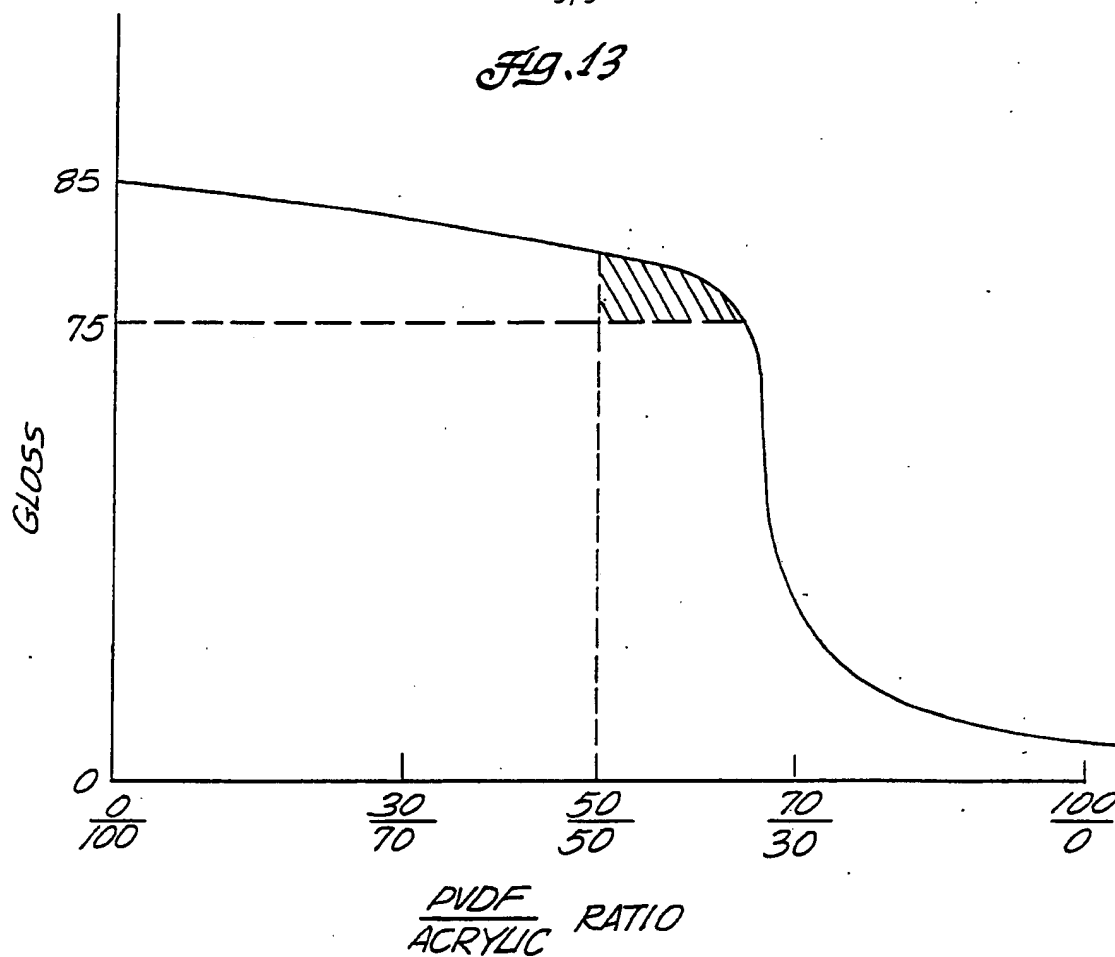
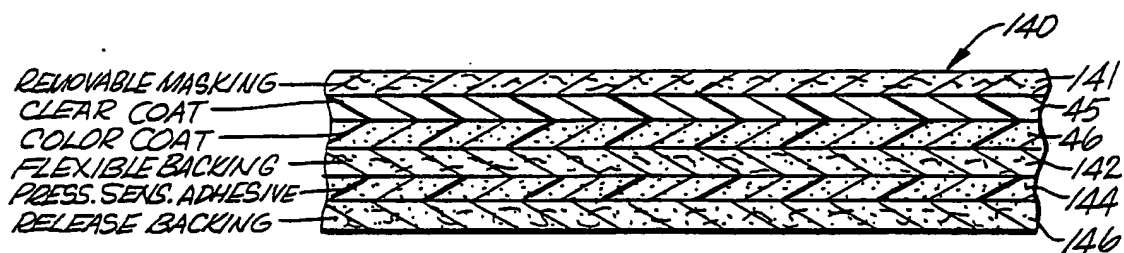


Fig. 14



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 88/00991

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : B 05 D 1/00; B 05 D 7/02; B 05 D 5/06; B 62 D 29/04; B 44 C 3/04; B 44 C 3/08; B 44 C 5/04																				
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; text-align: left; border-bottom: 1px solid black;">Classification System</th> <th style="text-align: left; border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px;">IPC⁴</td> <td style="padding: 5px;">B 05 D; B 44 C; B 60 R; B 62 D; B 60 J</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁴	B 05 D; B 44 C; B 60 R; B 62 D; B 60 J														
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IPC ⁴	B 05 D; B 44 C; B 60 R; B 62 D; B 60 J																			
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; text-align: left; border-bottom: 1px solid black;">Category ⁹</th> <th style="text-align: left; border-bottom: 1px solid black;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="text-align: left; border-bottom: 1px solid black;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">US, A, 4307058 (E.B. MORELLO) 22 December 1981 see column 1, line 58 - column 2, line 29 --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,7,20,26</td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0109313 (NEVAMAR) 23 May 1984 see page 2, lines 11-35; page 7, lines 3-31 --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-3,5,6, 12,14,17, 20-23,25,26,32</td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0133119 (ACIERS ET OUTILLAGE PEUGEOT) 13 February 1985 see page 2, lines 7-16 --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,7,20,26, 50</td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">Automobiltechnische Zeitschrift, volume 84, no. 5, May 1982, (Schäbisch Gmünd, DE), "Heissprägefolien und Heisspräge- maschinen", page VIII see the whole abstract --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,2,20-22</td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">Plastics World, November 1986, B. Miller: "Composite structures: Next wave in Detroit, see pages 30-34</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,20,21</td> </tr> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	US, A, 4307058 (E.B. MORELLO) 22 December 1981 see column 1, line 58 - column 2, line 29 --	1,7,20,26	A	EP, A, 0109313 (NEVAMAR) 23 May 1984 see page 2, lines 11-35; page 7, lines 3-31 --	1-3,5,6, 12,14,17, 20-23,25,26,32	A	EP, A, 0133119 (ACIERS ET OUTILLAGE PEUGEOT) 13 February 1985 see page 2, lines 7-16 --	1,7,20,26, 50	A	Automobiltechnische Zeitschrift, volume 84, no. 5, May 1982, (Schäbisch Gmünd, DE), "Heissprägefolien und Heisspräge- maschinen", page VIII see the whole abstract --	1,2,20-22	A	Plastics World, November 1986, B. Miller: "Composite structures: Next wave in Detroit, see pages 30-34	1,20,21
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IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-right: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search 18th August 1988 </td> <td style="width: 50%; padding: 5px;"> Date of Mailing of this International Search Report 06 SEP 1988 </td> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px;"> International Searching Authority EUROPEAN PATENT OFFICE </td> <td style="padding: 5px;"> Signature of Authorized Officer P.C.G. VAN DER PUTTEN </td> </tr> </table>			Date of the Actual Completion of the International Search 18th August 1988	Date of Mailing of this International Search Report 06 SEP 1988	International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer P.C.G. VAN DER PUTTEN														
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
	cited in the application --	
A	EP, A, 0178096 (DU PONT) 16 April 1985 see page 8, lines 14-33 & US, A, 4692481 (cited in the application) --	3,8,9,22
A	WO, A, 81/00233 (DU PONT) 5 February 1981 see page 1, lines 1-18; page 7, lines 27-35 -----	1,16,20

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8800991
SA 22810

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4307058	22-12-81	CA-A- 1156811	15-11-83
EP-A- 0109313	23-05-84	JP-A- 59162042	12-09-84
		US-A- 4517235	14-05-85
		US-A- 4520062	28-05-85
		CA-A- 1235340	19-04-88
EP-A- 0133119	13-02-85	FR-A,B 2549418	25-01-85
		JP-A- 60073812	26-04-85
EP-A- 0178096	16-04-86	JP-A- 61085481	01-05-86
		US-A- 4692481	08-09-87
WO-A- 8100233	05-02-81	EP-A- 0033725	19-08-81